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PERFORMACE OF UREA-BASED IN-SITU CO2 EOR: INFLUENCES OF DIFFERENT POROUS MEDIA

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PERFORMANCE OF UREA-BASED IN-SITU CO2 EOR: INFLUENCES OF DIFFERENT POROUS MEDIA

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BY

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Table of Contents

Lists of Tables

Lists of Figures

Abstract

Carbon dioxide (CO_2) flooding has been proved as a successful method for enhanced oil recovery (EOR) in oil fields globally in recent decades. However, significant growth of applying CO_2-EOR technology is largely restricted by factors such as limited natural source of CO_2 and transportation, viscous fingering, gravity override at the reservoir and corrosion of equipment. To avoid some of these limitation issues, an improved in-situ CO_2 gas generation technique for EOR was studied in this thesis research work, through a series of controlled laboratory scale experiments under various in-situ conditions. In this work, urea was chosen as potential CO_2 generation candidate, because of its exceptional high aqueous solubility, and robust decomposition mechanisms to carbon dioxide and ammonia products at appropriate reservoir conditions. Once formed, the produced CO_2 in aqueous brine easily migrates to the trapped oil phase due to its rather high solubility in oil. These ongoing mass transfer processes cause oil phase swelling and decreasing oil viscosity, therefore results in significant increase of oil production. At the meantime, the dissolved ammonia generated in the aqueous phase would offer additional benefits similar to that of a common alkaline injection. Ammonia could react with polar petroleum acids in crude to produce surfactants in-situ which not only decreases the interfacial tension between oil and water, but also leads to a better sweep efficiency as a result of emulsion generation. Meanwhile, the alteration of wettability in both sandstone and carbonate rocks was evidenced at elevated alkalinity.

Performances of urea-based tertiary recovery were conducted in a series of flow-through tests maintained at back pressure of 1500 psi and temperature of 125 ^{o}C. Several light crude oils (API around 40) and pure dodecane were used as representative oil system. The chemical concentrations of injecting urea and single alkaline, ammonium hydroxide, were pre-determined at 35 wt% and 15 wt%, respectively. After reaching the residual oil saturation following initial (sea)water flooding, the chosen steps of 1+1 pore volume of chemical slug injection were executed sequentially into the steel column device and immediately followed by two shut-in cycles, each shut-in cycle lasted 72 hours. The best tertiary recovery performance was recorded in sandstone media, varying from 5.17% to 26.09%, followed by the cases of limestone, ranging 0% to 12.37%, and the least dramatic in case of dolomite, close to 9.72%. The predominant mechanisms of urea-based EOR formulations observed in this study involve oil swelling, viscosity reduction, IFT decreasing and wettability alteration. Regardless of the types of porous media used, injection of urea was capable of dramatically enhancing oil recovery as compared with those of conventional water floodings, and even competing with a regular supercritical CO_2 flooding. It is worthy to note that tertiary recovery in carbonate formations might not be as drastic as that in sandstone media. Overall, proper design of urea-based in-situ CO_2 system may potentially offer a superior EOR alternative to be applied in both onshore and offshore oil fields.

Chapter 1: Introduction

1.1 Overview

According to the annual energy outlook 2018 report from US. Energy Information Administration (EIA), the fossil fuels are expected to meet the most energy consumption around the world from 1980 to 2040. The shares of petroleum and natural gas resources increase more than other fuel sources, largely caused by increasing demands from the industrial and electric power [1]. The increases of relative cleaner natural gas and renewable energy generation led a net coal consumption decreases by 0.1% per year in the electric power sector. In addition, the average total global petroleum and other liquids consumption in 2018 is 100.1 million barrels per day and EIA forecasts it will continuously increase in the future. On the other hand, the average total global crude oil production reaches only 97.52 million barrels per day in 2018. Therefore, it is necessary to explore new oil fields and better technologies in enhancing oil recovery to meet growing demand in energy sources in the years to come.

The Improved Oil Recovery (IOR) methods may involve new drilling and well technologies, intelligent reservoir management and increasing the oil recovery of secondary and tertiary production by introducing external energies. In particular, the term of Enhanced Oil Recovery (EOR) is specifically designated for those technologies and engineered system involved in tertiary oil recovery. To date, the most common use EOR methods are thermal technology, which is largely preferred for many heavy oil reservoirs using steam injection. Thought their EOR potentials may be great, yet the

chemical (flooding) EOR method had made only a relatively small contribution to current global oil production because of their rather high capital investments and project costs, and instead gas injection method is a preferred choice for gas condensate reservoir and offshore field. Not surprisingly, the past and future commercial EOR projects around the world have strongly affected by crude oil price on the return of these investments. This thesis presents the combination (e.g. a hybrid system) of chemical flooding and gas injection method for enhancing tertiary recovery. It is well known that most EOR system are depending on the reservoir lithology which could limit the performance of specific EOR methods [2]. Figure 1-1 represents that 78% of EOR projects are carried out in sandstone reservoir, and in sandstone reservoirs, thermal and chemical methods are most frequently used compared to gas injection. However, the large portions of global crude oil are stored in

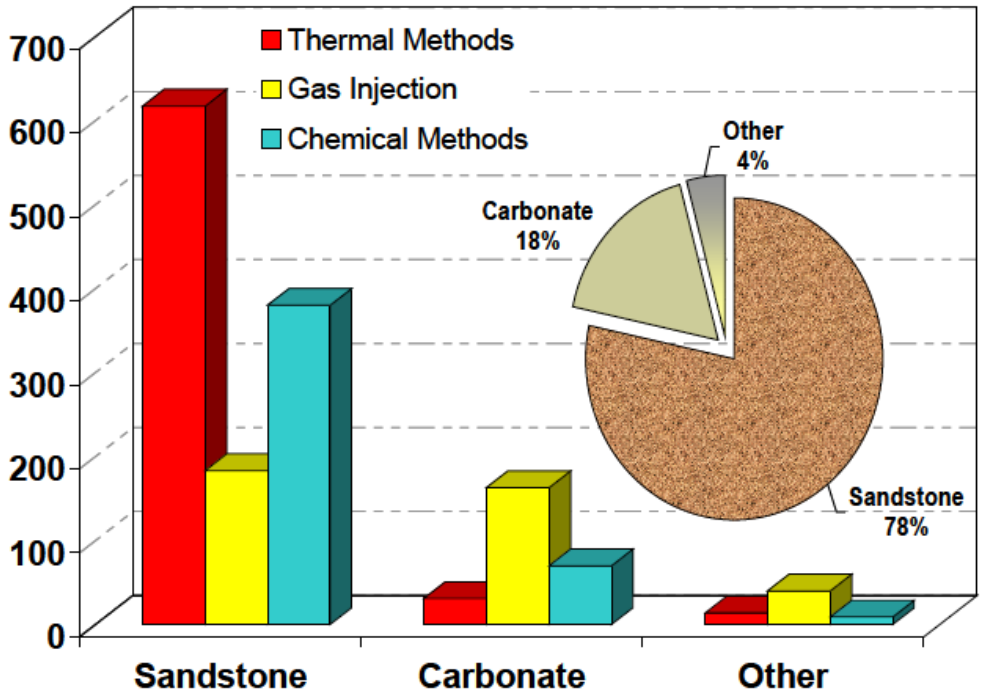

Figure 1-1 Different EOR methods used by reservoir lithology [2010 data, adopted from ref. 2]

carbonate formations which are currently applying gas injection as the most common EOR process in those fields. Because of low porosity and tight permeability exhibited in this type of lithology and rather complex surface wettability, i.e., oil to mix wetting, the resulted oil recovery rate in the carbonate rocks are typically quite low, so choosing optimum EOR methods is significantly critical and challenging. Whereas, the EOR in offshore reservoir is more limited than the onshore ones, because the offshore EOR project is not only constrained by reservoir lithology, but also by tight space of surface facilities and environment considerations of any waste disposal.

1.2 Enhanced Oil Recovery by CO_2 flooding

The carbon dioxide (CO_2) as the greenhouse gas is released into the atmosphere by combustion of fossil fuels such as oil, natural gas and coal. Moreover, excessive release of these greenhouse gases will cause the global warming and seawater level rising [3,4]. Consequently, the engineering captured CO_2 from the natural or man-made sources and large industrial facilities should be securely stored as one of the alternative to mitigate these climate change issues. Over the years, the Permian Basin in the United States has rich quantities of CO_2 from both natural and industrial sources. There were numerous successful applications of the CO_2-EOR process in that region because of two main advantages: additional hydrocarbon recovery and CO_2 sequestration and storage operations to reduce the atmospheric emission of CO_2 [5,37]. On the other hand,

because of the unique properties of CO_2, the predominant mechanisms of CO_2-EOR are swelling the crude oil, decrease of oil viscosity, lowering interfacial tension, and mobilizing the lighter components of the crude oil. The injected CO_2 can operate either at multiple-contact miscible mixing or immiscible mixing with the trapped oil, depending on the reservoir pressure and injection conditions. In general, miscible CO2 flooding is preferred in reservoir because it can achieve higher recovery than that of immiscible process. According to previous work done at this group, conducting flow-through sandpack tests above the minimum miscibility pressure (MMP) was not a critical parameter of in situ CO2 flood to achieve a better tertiary recovery [8,38]. So, in this work, the designed backup pressure was set at 1500 psi, which is below the MMP. Also, because of viscous fingering and gravity override, the injected CO_2 may breakthrough too rapidly and cause significant poor sweep efficiency especially in carbonate media. Previously, adoption of water-alternating-gas (WAG) process for CO2 EOR could partially overcome this issue [7]. In the light oil reservoir where the formation pressure is above the MMP, the WAG injection system offers some operational advantages. Firstly, it leads to higher oil recovery than waterflooding and miscible CO_2 flooding because of improvements made in both volumetric sweep efficiency and displacement efficiency. Then it can significantly reduce total CO_2 consumption and project capital and operations costs as compared to continuous injection of miscible CO_2 flooding [9,11]. However, in cases of thicker formations, the WAG technology appears hard to become economically viable and increasing technical difficulties for implementation. Some of the challenges are related to better determining

the optimal WAG injection parameters, such as WAG slug size, the WAG slug ratios and fluid injection sequence in each cycle. Therefore, to control these adverse inefficient issues and maximize the oil recovery, Carbonated Water Injection (CWI) approach was introduced by others. In CWI operations, the CO_2 is first dissolved into the aqueous phase and delivered into the reservoir, then it increasingly migrates into the trapped oil phase because of apparent high solubility of CO_2 in the oil phase, e.g., the amount is 3 to 7 times greater than that in aqueous phase under similar condition of pressure and temperature. This mass transfer phenomenon causes the oil phase to become highly mobile and swelling, effectively increasing total volume of oil while decreasing both oil viscosity and water-oil interfacial tension, even up to 20% [12,13,39]. After the amount of CO_2 reaching equilibrium between oil and aqueous phase, the resulted swelling factor (SF) is defined as the volume of the oil and dissolved CO_2 divided by the volume of the oil without CO_2 [15]. Thus, comparing with conventional water-only injection, the CWI improves oil recovery in secondary and tertiary production. The carbonated water injection (CWI) is more attractive to offshore reservoirs or other reservoir with limited access to CO_2 [14]. In this work and being distinct different from a regular CWI, the much concentrate CO_2 plume was generated by urea decomposition in situ at high temperature, and the mass transfer of CO_2 between the aqueous phase and oil phase can be determined by partition coefficient which is the ratio of CO_2 solubility in water and oil [16].

1.3 In-situ CO_2 EOR Technology

It is known that the pure carbon dioxide is relatively expensive than other displacing fluids; depending from source, CO_2 varies from $0.65/MCF to $3/MCF. So, when the oil price drops significantly, it makes CO_2 flooding uneconomical [17]. Moreover, there are some adverse operational factors restraining wide application of CO_2-EOR. First, CO_2 is easily breakthrough to oil production wells, and then in presence of moisture, it can trigger wells, field equipment and transportation pipeline corrosion, this significantly increases the site operations and maintenance cost. Therefore, development of new improved technologies such as in-situ carbon dioxide generation to eliminate any surface facility problems and negative impact is imperative [18,19].

The technologies of in-situ CO_2 generation for EOR can be classified as improving displacement efficiency and sweep efficiency. Compared with conventional supercritical CO_2 flooding, there is no need for availability of near-by natural or industrial CO_2 sources by in-situ CO_2 method. The containers of concentrated reagents can be transported to the field and get diluted on the job site conveniently. Thus, it is especially beneficial for applying at remote locations. Also, there is less requirement for surface equipment such as compressor, power supplies and installation of new pipelines, therefore leads to less cost compared to conventional CO_2 flooding. If success, this technology results in increasing oil production and injectivity of wells, reducing water cut and injection pressure for secondary and tertiary recovery [19,20]. In this work based on prior efforts done at this group, the concentrate urea was selected as in-situ CO_2 gas generation agent; once injected, it produced adequate amount of CO_2

required in the steel column test when temperature reached a threshold value of 80^{o}C and above.

1.4 Gas generation agent Urea

Urea (NH_2CONH_2) is a nontoxic chemical compound; it is no danger to the environment, animals, plant life and human beings. At the ambient temperature and pressure, it exists as solid phase [41]. Most importantly, urea is highly soluble in fresh water (1080g/L at 20^{o}C) or brine. Consequently, urea can be transported safely and conveniently in bulk quantity and stored for extended period. On the other hand, with slow addition of thermal energy, the decomposition of urea solution sharply increases at temperature approaching 80^{o}C; so ideally, at high temperature reservoirs, the injected urea will hydrolyze in aqueous solution once reached thermal equilibrium deep in the formation and then generate the desired carbon dioxide and ammonia simultaneously. The basic chemical reactions in the hydrolysis of urea follow a two-step procedure [21-23]:

$$NH_2CONH_2 + H_2O \rightarrow NH_2COONH_4 \quad \text{(1.1)}$$

$$NH_2COONH_4 \rightarrow 2NH_3 + CO_2 \quad \text{(1.2)}$$

The reaction in Eqn. 1.1 is mildly exothermic as urea hydrolyzed in water to form ammonium carbamate. However, the Eqn 1.2 is strongly endothermic with ammonia and carbon dioxide generation. It can be concluded that the hydrolysis of urea to generate these two gases is a pseudo first-order reaction, and the initial reaction rate is slow until temperature increases to around 130 ^{o}C.

Ammonia is an important chemical which is widely used in industry and utility. Ammonia dissolves in water to form ammonium hydroxide, a weak base solution that provides alkalinity [24,40]. The equilibrium reaction can be expressed:

$$NH_3 + H_20 \rightleftharpoons NH_4^+ + OH^- \quad \text{..... (1.3)}$$

Ammonia has been suggested as Alkali/Surfactant/Polymer (ASP) flooding agent in the crude oil which contains polar components such as petroleum acids, bitumen and asphaltene. One of the mechanisms of alkaline flooding is alkaline reaction with these polar components in the crude oil to produce surfactant soaps in-situ that effectively lower the interfacial tension between oil and aqueous phase [25]. The reaction of in-situ surfactant generation is expressed as follows,

$$HA + OH^- \rightleftharpoons A^- + H_20 \quad \text{..... (1.4)}$$

Where HA is petroleum acid in the oil phase which migrates to the O/W interface and converts to anionic surface-active agent A^- at high pH and leads the lower IFT for releasing the trapped oil [26]. Chapter 2 will cover the results of IFT measurements between the alkaline solution and crude oil. However, lowering IFT alone is not sufficient to improve oil recovery. The in-situ generated surfactants also form water-oil emulsion, which is likely re-trapped in porous media downstream. The occurrence of entrapped emulsions can lower the injected water mobility and further increase the sweep efficiency. In addition, the alkali provided by ammonium hydroxide has faster induction time to release bitumen than sodium hydroxide at the same level of pH, which has been proved by Wang et al in laboratory sandpack tests [21]. In Chapter 3, we

report the effect of alkali on enhancing tertiary recovery in both sandstone and carbonate rocks. It is believed that the ammonium hydroxide has similar performance on carbonate rocks evaluated, which is attributed to carbonate rock surface to liberate bitumen. Overall, ammonium hydroxide was found to be a suitable substitute for sodium hydroxide [27].

Another important mechanism for EOR is wettability alteration. The evidence shows water-wet sandstone surface has wettability reversal due to ammonia used [8,21]. Whereas, it is known that carbonate reservoir is typically under neutral wet to oil wet situation. This is because the polar compounds asphaltenes and organic acids in the crude oil has polar end which contacts the positive charge of carbonate surface and the hydrocarbon long chain expose loosely to the aqueous phase, making the solid surfaces more oil wet [29]. The processes of in-situ surfactant generation by alkaline flooding not only can reduce interfacial tension (IFT) effectively but also change wettability of media by liberating polar components in crude [30-33]. In Chapter 3, the tertiary recovery was analyzed in a series of flow through tests in various sandstone and different carbonate media (limestone and dolomite). Wettability alteration plays a crucial role in EOR especially in oil-wet carbonate. It is reported that divalent ions in seawater had the ability to change carbonate rock wettability [34-36]. The presence of dissolved CO_2 in the seawater results in more wettability alteration in limestone than dolomite and the detailed results will be given in Chapter 3.

To sum up, the benefits of in-situ CO_2 based on addition of urea include:

I. Eliminating negative effects of supercritical CO_2 flooding (sources, installation, corrosion and transportation issues).

II. Better sweep efficiency than conventional CO_2 flooding process.

III. Improving significant tertiary recovery even under the sub-minimum miscibility pressure condition.

IV. Reasonable simple setup and cheap raw materials used in the formulations.

Chapter 4 leads to the conclusion of the thesis research and recommendations for future effort and endeavors.

Chapter 2: Alkaline solution/Oil system for Interfacial tension measurement

2.1 Materials

2.1.1 Chemicals

Urea (purity, 99 w.t%) and Sodium hydroxide (purity 97 w.t%) were purchased from the ACROS ORGANICS and Sigma-Aldrich, respectively. Three types of oil were used for interfacial tension (IFT) measurement, two crude oil were donated from ADNOC (Middle East) and Arrow Oil and Gas (Norman, OK) and one pure n-alkane, dodecane, purchased from Sigma-Aldrich.

2.2 Experiment Setup

The experiment was designed for room temperature and atmospheric pressure by using axisymmetric drop shape analysis (ADSA) for liquid-liquid surface tension measurement. The ADSA model-CAM 101 (KSV Instruments Ltd, Finland) is an image analysis of surface tension from pendant drop model. The images are recorded by camera and analyzed by drop shape software. The Figure 2-1 shows the schematic of ADSA setup. The syringe was filled with lighter oil phase which injected into the connection line and needle by using Teledyne Isco pump to control the constant volume. And quartz cuvette was filled with equilibrated aqueous solution. After allowing enough time lapsed to achieve stability at the interface, the camera recorded

oil drop shape image and then calculated the interfacial tension by software using Young-Laplace theory.

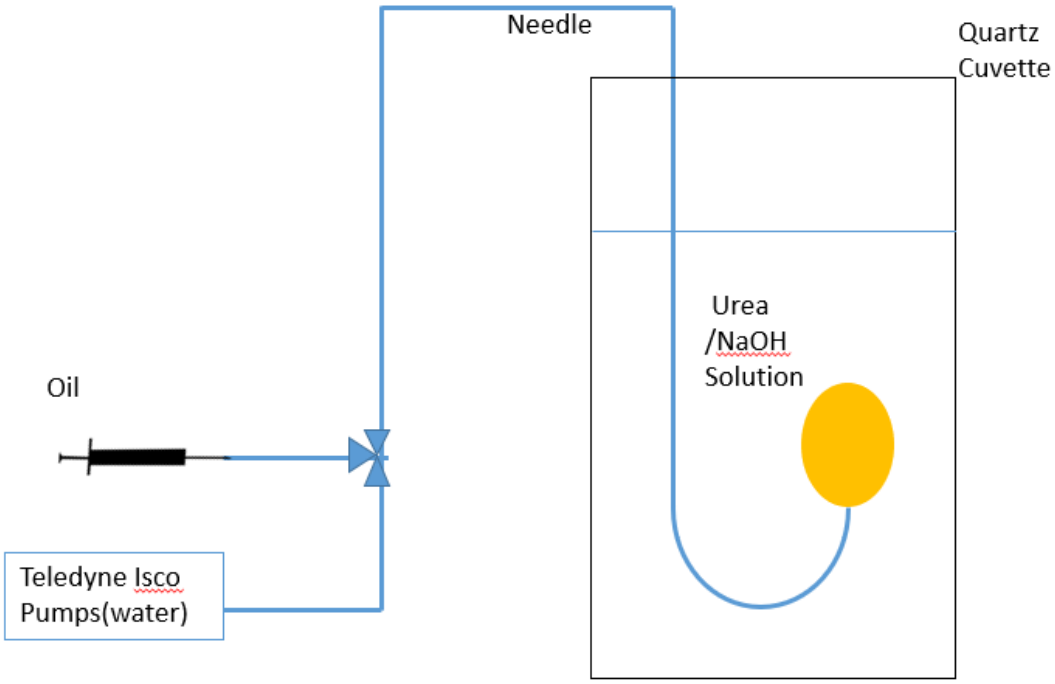

Figure 2-1 Schematic of ADSA setup

2.3 Experiment Procedure

The alkaline solutions were prepared by diluting the urea and sodium hydroxide into target concentration. Each sample contains 15g of aqueous phase with 15 ml of oil. Samples were well mixed by using the vortex and then using shaker to rotate 14 days to reach the reaction equilibrium. Figure 2-2 was the shaker used in sample preparation.

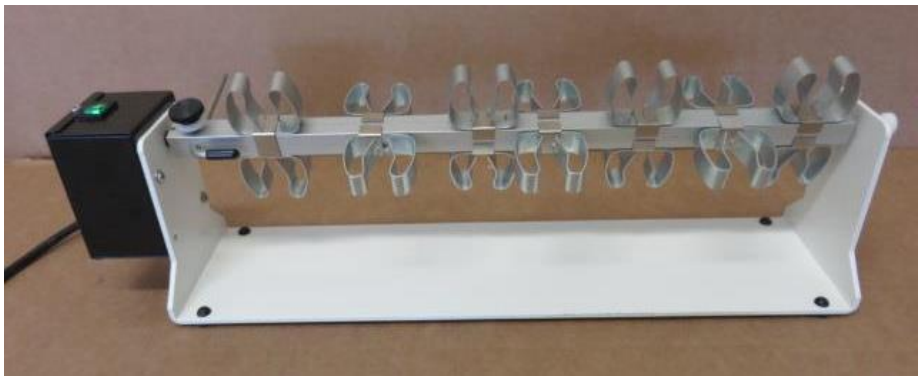

Figure 2-2 shaker used for samples equilibrium in IFT measurement

After samples reaching equilibrium, there were two input data for axisymmetric drop shape analysis (ADSA) software with pendant drop model, which were density and molecular weight of lighter phase and heavier phase. Next, quartz cuvette was filled by heavier phase which was transferred from the bottom of the equilibrated samples and caution was taken to avoid mixing with any oil. Then lower down the J-shape needle until close to bottom of cuvette. Slowly injected lighter phase which was taken from the top of equilibrated samples using a clean syringe and all the lines need to be filled with oil until the first oil drop came out from the needle. To get constant oil drop volume for consistent analysis, the Teledyne Isco pump was adopted to precisely maintain the volume of the oil droplet at 4 μL. Allowing adequate time to achieve stability at interface between the heavier phase and oil drop. Once the oil drop shape reaching the equilibrium, the camera recorded 10 second animation at 6 frames per second. The ADSA software would automatically detect the edge of the oil drop and calculate interfacial tension, but one of the issues by using this method was image noise. The sample drop image presented on the monitor screen, the edge of the drop would be

black, and the background would be clear white. However, because of the complex composition of crude oil, the surrounding fluid was not completely clear white, and a sharp distinction between drop edge and the surrounded fluid may not present. As a result, it would decrease the accuracy of detecting drop edge by camera. So, it had to be very careful to transfer heavier phase into the cuvette and allow enough time to get background stable.

2.4 Results and Discussion

Urea has a very high solubility in water (1079g/L at 20^{o}C), and it hydrolyzes in aqueous solution at relatively high temperature. Urea will decompose to ammonia and carbon dioxide, then the ammonia will dissolve in water to form a weak base ammonium hydroxide to provide alkalinity.

The alkali flooding can significantly increase the oil recovery in water-wet sandstone reservoir than in oil-wet carbonate reservoir by reducing the interfacial tension and reverse the wettability. The Figure 2-3 indicates the interfacial tension measurement for equilibrium solution of sodium hydroxide with two different crude oils. The crude oil samples likely contain bitumen and asphaltene which have polar components such as long-chain carboxylic acids. Due to the chemical reactions between alkali and organic acid, it will generate surfactant based on following equation:

$$HA + OH^{-} \longleftrightarrow A^{-} + H_2O \quad \text{..... (2.1)}$$

The HA represents organic acid from crude and A^{-} is a surface-active agent or surfactant.

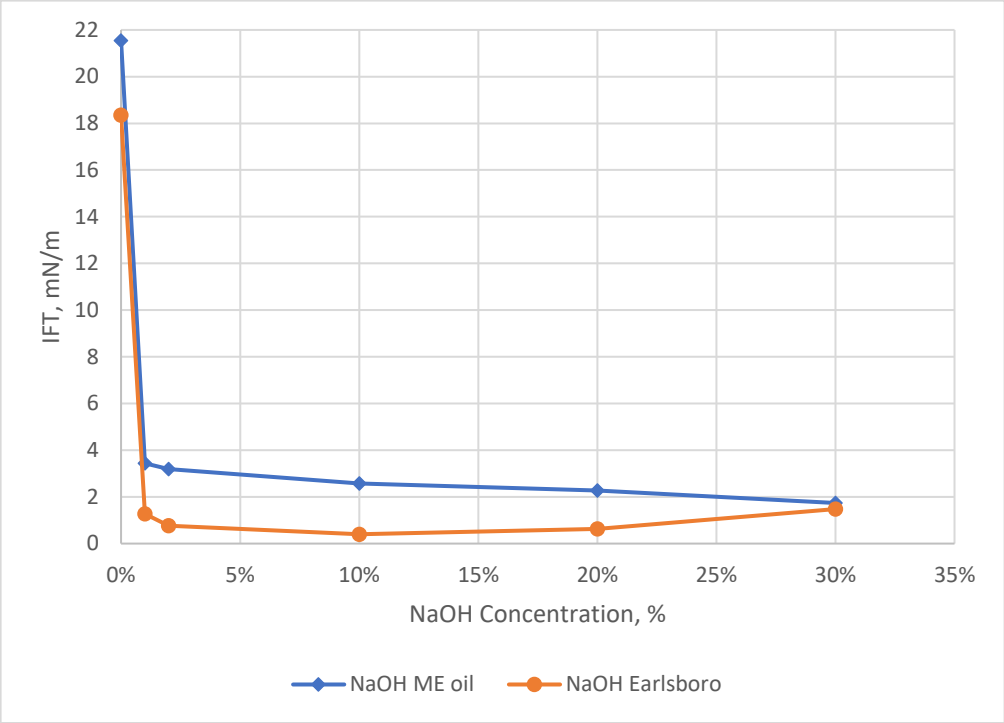

Figure 2-3 Interfacial tension for sodium hydroxide with Middle East oil and Earlsboro oil

It is observed that the interfacial tension decreases with increasing concentration of NaOH for Middle East oil. However, for Earlsboro oil, once IFT decreases to minimum value with 10% NaOH, then it slightly increases when further increases NaOH concentration. Wasan [26] introduced a characteristic parameter, K, i.e., the ratio of the ionized/ un-ionized acids, which governs the effects of interfacial tension change. If K equals to 1, IFT can go through a minimum value. The initial reduction of the interfacial tension is because of increasing concentration of NaOH, it causes the balance Eqn. 2.1 shifting to the right, and more ionized acid, A^- being generated at the interface. In addition, when continuously raise NaOH concentration, the un-ionized acid

concentration decreases very quickly after reaching the minimum IFT. The IFT increasing is due to flux of ionized acid away from the interface is faster than the flux of un-ionized acid toward the interface. So, the interfacial tension was found to reach the minimum in lower concentration of NaOH. Rudin and Wasan measured interfacial tension between Long Beach crude oil and alkaline solution of NaOH. It shows the transient IFT as a function of pH for different levels of total sodium. Figure 2-4 shows similar trend as this work. The minimum IFT shifts to lower pH and increases for higher alkali concentration.

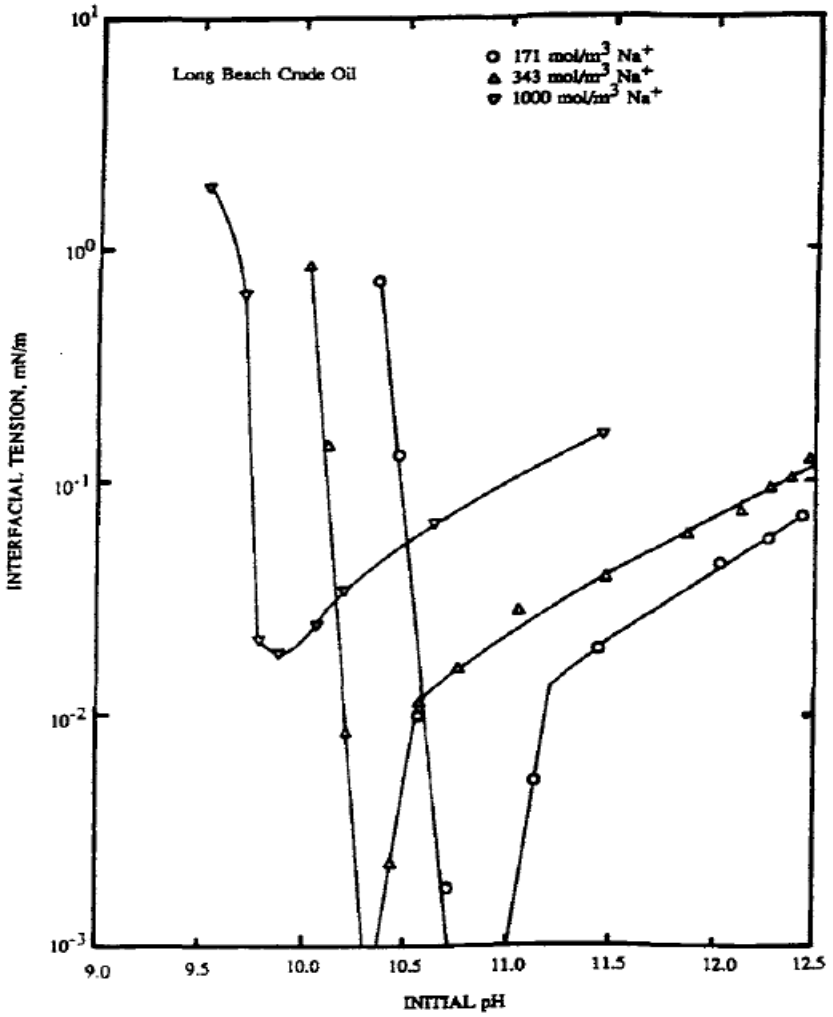

Figure 2-4 Effects of sodium on interfacial tension at different pH alkaline solution [data adopted from ref. 26]

The material of urea itself is a neutral substance, however, when it is hydrolyzed in aqueous solution, it will slowly form ammonium carbamate as equation 1.1. Because the two nitrogen atoms in urea structure, H2N-C=O-NH2, both have unpaired electrons, they are more available interacting with free protons (H^+) in water. As a result, the rest of OH^- makes urea as a week base. What is more, the slight alkali concentration will

generate a little bit of surface-active agent, it leads IFT to drop by equation 1.4. In Figure 2-5, the interfacial tension reduces slightly for two different oil as increase the concentration of urea at room temperature and atmospheric pressure.

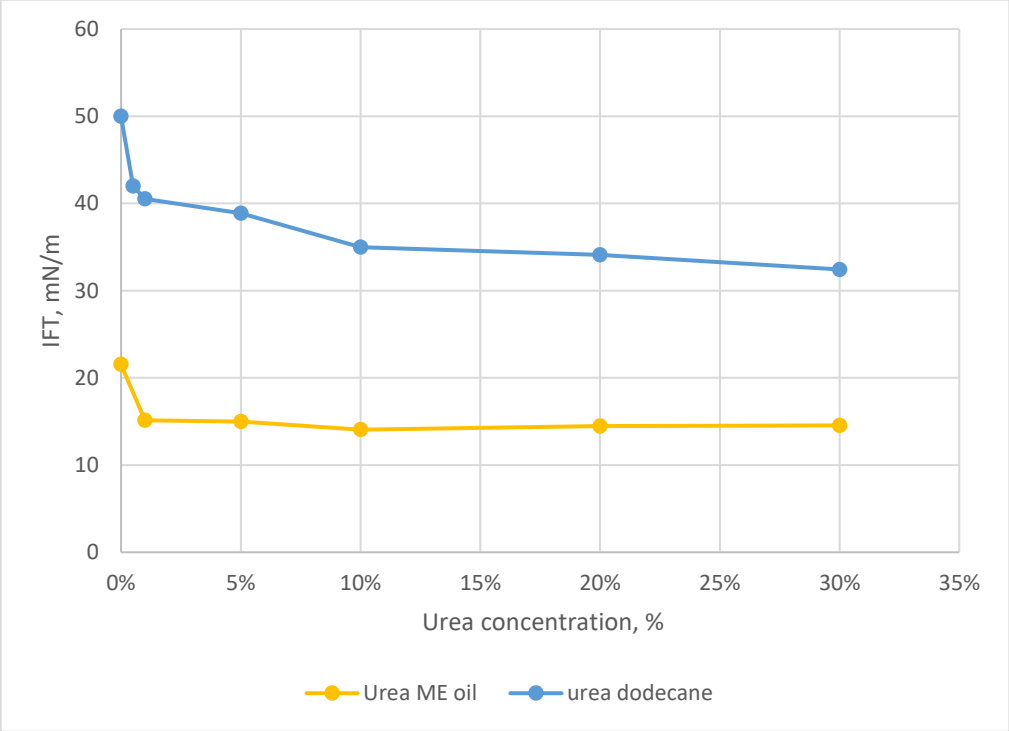

Figure 2-5 Interfacial tension for Urea with Middle East oil and pure Dodecane oil

Comparing crude oil with pure dodecane, the polar components in crude oil will cause a lower IFT by surfactant generation. However, because of the weak surface activity of urea itself in aqueous solution at room temperature, the IFT in dodecane oil also decreases to a decent degree. Only at relatively high temperature will urea decompose and liberate sufficient ammonia to provide higher concentration of alkali. Thus, the IFT significantly decreases in NaOH alkaline solution than urea only at room temperature.

Chapter 3 Urea-based CO2 Generation EOR for Different Porous Media

3.1 Materials

3.1.1 Chemicals

The chemicals used for preparing artificial seawater were purchased from the Sigma-Aldrich, sodium chloride (purity 99.5 wt.%), magnesium chloride (purity 98 wt.%), potassium chloride (purity 99 wt.%), magnesium sulfate (purity 99 wt.%). And calcium chloride (purity 99%) was purchased from ACROS ORGANICS. Moreover, the chemical slug for gas generation urea (purity 99 w.t%) and ammonium hydroxide (purity 30 wt.%) were purchased from the ACROS ORGANICS and Sigma-Aldrich, respectively. The composition and concentration of the artificial seawater is listed below (**Table 3**-1)

Chemical	Concentration, wt%
NaCl	2.629
KCl	0.074
CaCl2	0.099
MgCl2	0.609
MgSO4	0.394

Table 3-1 Composition of Artificial Seawater

Two types of oil were used in the test, the pure dodecane purchased from Sigma-Aldrich and Middle East crude oil which was provided from ADNOC (Middle East). The physical properties of these two types of oil are listed below (**Table 3-2**)

	Dodecane	Middle East oil
API	57.3	38
Viscosity, cp	1.34	2.1
Density, g/ml	0.75	0.834

Table 3-2 Physical properties of the Dodecane and crude

3.1.2 Rock samples

Three different types of rock were used in this experiment, Ottawa sand F-75 was purchased from U.S. silica and Indiana limestone and Silurian Dolomite outcrops were purchased from Kocurek Industries. The original size of Ottawa sand is in the range of 75 μm to 600 μm and d50 is 150 μm. In order to get consistent result, the Ottawa sand, Indiana limestone and Silurian dolomite were crushed and sieved; the porous media size between 106-250 μm were collected and used in the flow-through experiments. The Table3-3 exhibits the composition of testing rock samples.

	Composition	Homogenous
Ottawa Sand F-75	99.7% Silica (Quartz)	Yes
Indiana Limestone	98% Calcium Carbonate	Yes
Silurian Dolomite	99% Dolomite, 1% Calcite	No
Porous Media, μm	106-250	

Table 3-3 Composition of rock samples used in the flow-through experiments

3.2 Experiment Setup

This experiment was designed at reservoir temperature 120^{o}C and reservoir pore pressure 1500 psi. The Figure 3-1 shows the schematic of flow-through test setup. There were two syringe pumps used to provide high pressure, one for fluid injection and another one for adjusting back pressure. Three accumulators filled with urea, ammonia hydroxide and artificial seawater, respectively. The flow-through columns were made

by stainless steel and were heated up by oven during the test. The inside diameter of stainless column is 0.834 inches and the pressure, temperature rating can go up to 3100 psi and 200^{o}C, respectively. A digital thermometer would automatically record oven temperature. Two digital pressure gauges continuously record pressure between inlet and outlet of the flow-through column. At the end of the test, the temperature and pressure data can be collected for further analysis. Backpressure regulator was connected before the effluent. The liquid and gas were collected by a sealed burette and graduated cylinder. In addition, the volume of the oil and gas were recorded manually by reading the liquid level change.

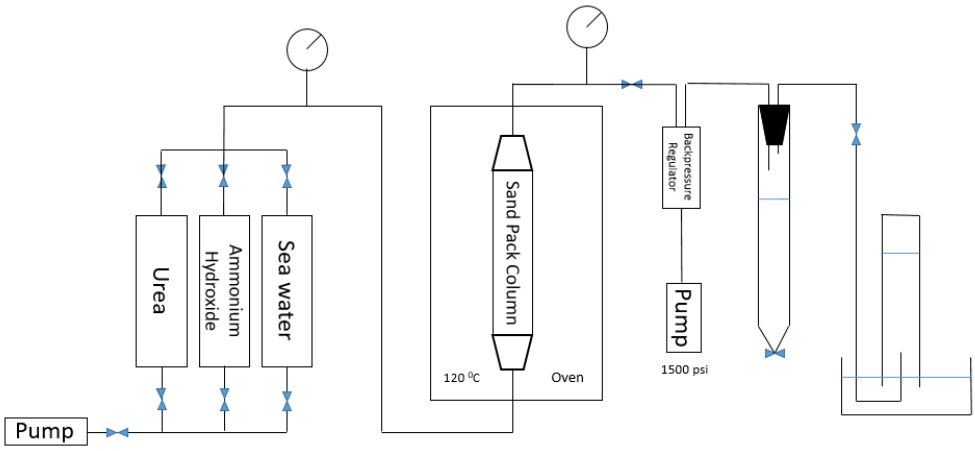

Figure 3-1 Schematic of flow-through test

3.3 Experiment procedure

Artificial seawater was pre-prepared with deionized water, and gas generation agent urea solution (35 wt.%) was also pre-prepared in artificial seawater. Moreover, ammonium hydroxide solution was diluted to 15 wt.% in deionized water. All of these

three solutions were carefully loaded into the accumulators and connected with pump (TELEDYNE ISCO D-SERIES) for pressure control. In order to have a consistent sample pack, a fixed amount of crushed sample, 90g, was packed into the 6-inch length stainless-steel column. Based on the experiment experience, the most significant issue for this test was leaking problem. So, when packing the rock sample into column, it had to be very careful and try to avoid any sample particles fell into the seal part. After dry packing process, a specific amount of crude oil or dodecane was injected into the stainless-steel column to saturate the sample using peristaltic pump in low injection rate 0.1ml/min. Because of different wettability of sandstone and carbonate rocks, the total injected oil volume would be different. Before start injecting solution, the total dead volume was measured for whole system as 23.9 mL. The inlet and outlet tubing should be filled with seawater before connected with stainless steel column. For this test, no aging process was adopted due to the limited time frame allowed for this work (though it is anticipated if longer aging process been used it would provide even better EOR performance for most cases). Therefore, after rock saturated by the oil, the seawater flooding was initiated. Firstly, before turning on the oven, the injection pressure was built up to 1500 psi in 3ml/min, then changed flow rate to 0.3ml/min and turned on the oven to 120^0C. Next injecting adequate seawater flooding 8-10 pore volumes to reach the residual oil saturation, until no more oil produced. Then 1 pore volume solution of urea or ammonium hydroxide was injected as chemical slug. In this test, the range of 1 pore volume for Ottawa sand was 18.95-21 ml, 25-26 ml for Indiana limestone and 23ml for dolomite. After injection of 1PV chemical slug, the test was shut-in for a 72-

hour cycle. The aim of the shut-in cycle was to allow the injected urea fully react with the rock surface and the trapped oil. After shut-in, post seawater flooding was carried out, until no more mobile oil produced. Then, additional one pore volume chemical slug was injected, and the second 72-hour shut-in cycle was initiated, followed by seawater post flooding continuously until no more mobile oil produced in the effluent. After the test, the oven was cooled down slowly, and two syringe pump pressures were carefully released. All the tubing lines and stainless-steel column needed to be cleaned before next run.

3.4 Results and discussion

Eight steel column tests were carried out with different porous media, while varying types of oil, and the selected reagents and concentrations for the new improved in-situ CO_2 generation method. The tertiary recovery was monitored as the key parameter for assessing the efficacy of in-situ CO2-EOR formulations. The main mechanism of this new method was a combination of carbonate water injection (CWI) and alkali flooding. The benefits of improved CWI in this system included oil swelling and oil viscosity reduction. Moreover, the alkali flooding had higher tertiary recovery due to in-situ surfactant generation and wettability reversal. So, these eight flow-through tests offered additional insights to the main mechanisms and important parameters. Based on previous study of Wang et al [8], the effect of injection flow rate and injection pressure were analyzed. The low injection rate of 0.3 mL/min was used in this test for longer chemical reaction time with porous medium. So, the gas generation urea hydrolysis and CO_2 mass transfer would adequately promote higher tertiary recovery. Also, applying

the concentrate urea solution of 35 wt.% will likely generate excessive amount of ammonia and CO_2, which can extract significant more of entrapped oil. According to literature reviews, the miscible CO_2 flooding would have better performance than immiscible CO_2 flooding. However, Wang et al. [42] reported that in situ CO_2 generation EOR by using urea above the minimum miscible pressure (MMP) did not show additional benefits of a miscible flooding. Table 3-4 shows result of below and above minimum miscible pressure effect on tertiary recovery.

Rock Type	Ottawa Sand	Ottawa Sand
Oil Type	Earlsboro	Earlsboro
Gas generation agent	Urea	Urea
Concentration, %	35	35
Flow rate, ml/min	0.03	0.03
Back pressure, psi	1500	4000
Tertiary Recovery, %	35.85%	15.80%

Table 3-4 Tertiary recovery at different backup pressure by using urea as gas generation agent with Earlsboro oil at 120ºC [42].

So, 1500 psi, which is below the MMP, was applied for back pressure. The Table 3-5 shows the test condition for Ottawa sand.

Test #	1	2	3	4
oil type	Dodecane	Dodecane	Middle-East oil	Middle-East oil
Brine	sea water	sea water	sea water	sea water
Chemical concentration, %	35% Urea	15% Ammonium Hydroxide	35% Urea	15% Ammonium Hydroxide
T, ºC	120	120	120	120

Back pressure, psi	1500	1500	1500	1500
Injection rate, ml/min	0.3	0.3	0.3	0.3
Sor	18.10%	27.62%	20.91%	14.54%

Table 3-5 Flow through column test condition for Ottawa sand (as mimic sandstone)

3.4.1 Ottawa Sand Tests

The oil saturation was plotted against the chemicals injection volume. Figure 3-2 shows the result of test #1, Ottawa sand with pure n-alkane dodecane and gas generation urea. The chemical slug, 35 wt.% of urea, was pre-prepared; artificial seawater was used for pre-flooding to approach the residual oil saturation (S_{or}), and post flooding was followed by shut-in process. From the Figure 3-2, after 6 PVs seawater flooding the S_{or} reached to 18.10%, which is represented by a red dash line. Two gray columns in the figure depicts two stages of chemical slug been injected. Once reached the Sor, 1 PV of 35 wt% urea was injected, in this sand pack 1 PV equals to 21mL. After 1 PV of urea slug injection, a 72-hr shut-in cycle was executed.

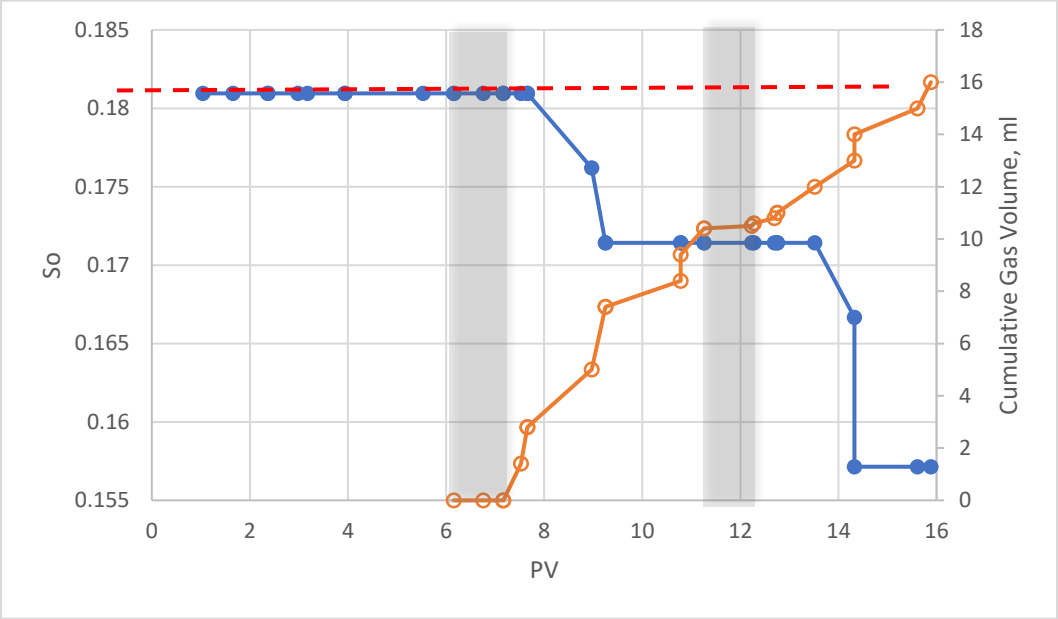

Figure 3-2 Oil saturation vs gas agent urea for Ottawa sand+Dodecane+35 wt.% Urea

The post flooding was immediately initiated at the end of the shut-in, the tertiary recovery (Etr) and oil saturation (So) can be calculated by using equation below:

$$\text{Etr} = \frac{\text{V } Produced\ oil\ from\ chemical\ slug\ injection}{\text{V } Dry\ pack\ oil\ volume - \text{V } Produced\ oil\ from\ seawater\ flooding} * 100\% \quad \text{.....(3.1)}$$

$$\text{So} = \frac{V\ Dry\ pack\ oil\ volume - V\ oil\ produced}{\text{V } pore\ volume} * 100\% \quad \text{..... (3.2)}$$

After second urea slug injection and shut-in cycle finished, the post seawater flooding was resumed until oil cut was zero. The tertiary recovery of first and second urea slug were 5.26% and 7.89%, respectively. The cumulative tertiary recovery was summed of two Etrs values, which was equal to 13.15%. The orange line represents cumulative CO_2 gas generated by urea decomposition. As we can see, the first cycle of urea

generated a similar amount of CO_2 with second cycle. In addition, the oil saturation started to decrease, i.e., beginning to produce oil, when urea started to generate CO_2. Moreover, in this test, most of the generated CO_2 dissolved into seawater and it transferred between the aqueous phase and trapped oil.

Figure 3-3 shows the test #2, which was Ottawa sand in the same pure n-alkane dodecane oil with ammonium hydroxide. The only difference between test #2 and test #1 was that chemical slug was replaced by non-gas generation agent ammonium hydroxide.

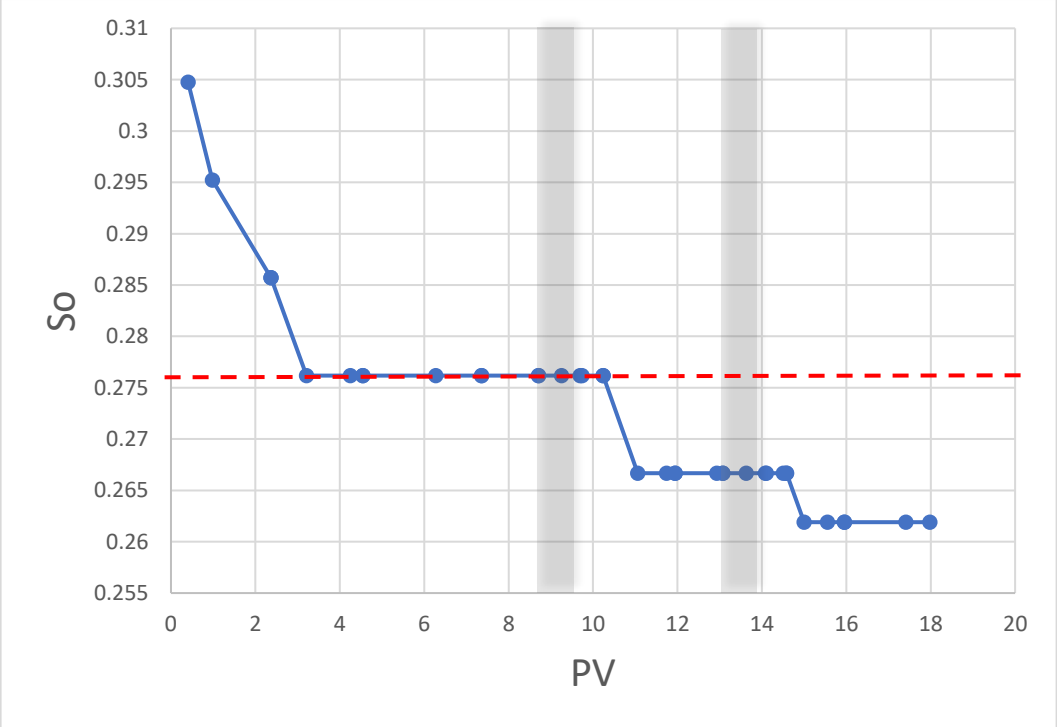

Figure 3-3 Oil saturation vs non-gas agent for Ottawa sand+Dodecane+15 wt.% ammonium hydroxide

15 wt. % of the ammonium hydroxide was used for chemical slug. The reason behind is that complete reaction of 35 wt% of urea, which was used in Test # 1, would generate equal amount of 15 wt% of ammonium hydroxide in high temperature. In order to isolate the predominant effects of CO_2 produced, the ammonium hydroxide-only system will provide single alkali effect. The adequate seawater pre-flooding reached the Sor 27.62%. After first chemical slug injected and shut-in cycle finished, the first Etr was 3.44%, and then resumed the seawater until no more dodecane produced. After that, followed by second chemical slug and shut-in cycle to get Etr 1.72%. The total tertiary recovery was 5.16%.

Figure 3-4 indicates test #3 using Middle East crude oil with 35 wt.% urea in Ottawa sand pack. Surfactant generation by polar component in crude is one of the significant mechanisms for EOR. Because of in-situ surfactant generation, the crude oil and pure n-alkane dodecane cases were used as fair comparison tests.

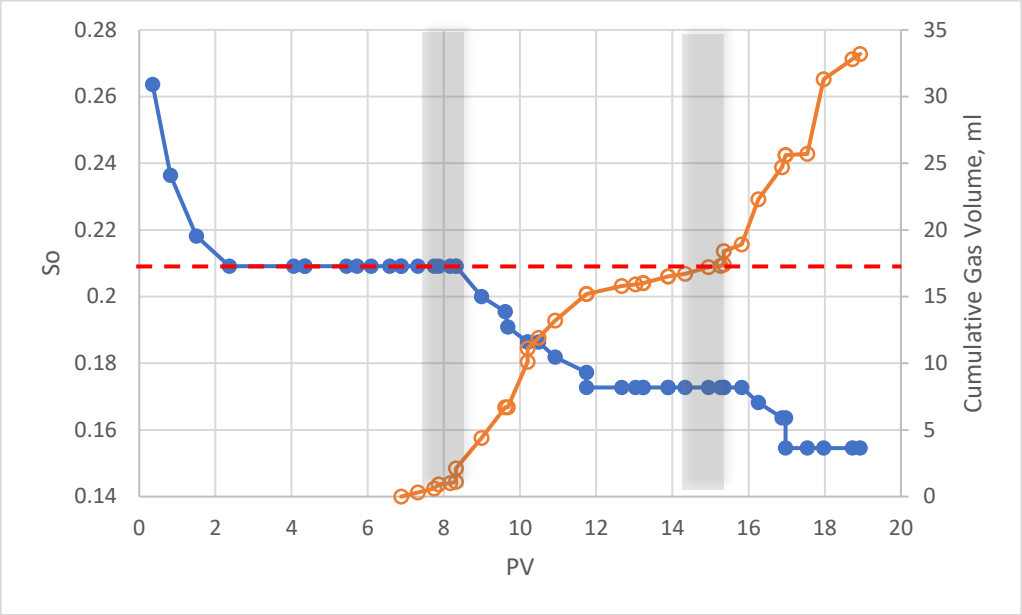

Figure 3-4 Oil saturation vs gas agent urea for Ottawa sand + Middle East oil+35 wt.% Urea

The test #3 firstly injected seawater for pre-flooding, the Sor was 20.9%. And then followed by first urea slug injection and 72-hours shut-in cycle. After shut-in process, resume seawater to get first urea injection recovery 17.39%. Next, the second 1 PV urea slug was injected with another shut-in cycle; after urea fully reacted with crude in high temperature, the second urea injection recovery was 8.69%. Therefore, the total tertiary recovery was 26.08% which was the optimal case with highest tertiary recovery observed in this work. Moreover, the orange line shows the cumulative CO_2 gas volume collected. In order to get consistent experiment results, it is important to avoid leaking issue in gas collection. It can be seen that, two similar slope of gas collection line proved the same amount of CO_2 produced during two stages urea slug injection. And it

will be further discussed in the latter section 3.4.4 with different rock media to achieve consistent CO_2 system.

Figure 3-5 shows test #4, the Middle East oil with 15 wt.% of ammonium hydroxide in Ottawa sand pack test. Comparing with test #3, it indicates the CO2 effect on EOR by using gas agent urea. Following the same procedure, 1 PV of chemical slug injection and 72 hours shut-in for each cycle. The Sor was 14.54% and the tertiary recovery were 6.25% and 3.125% for first and second ammonium hydroxide injection, respectively. The final total Etr was 9.375%.

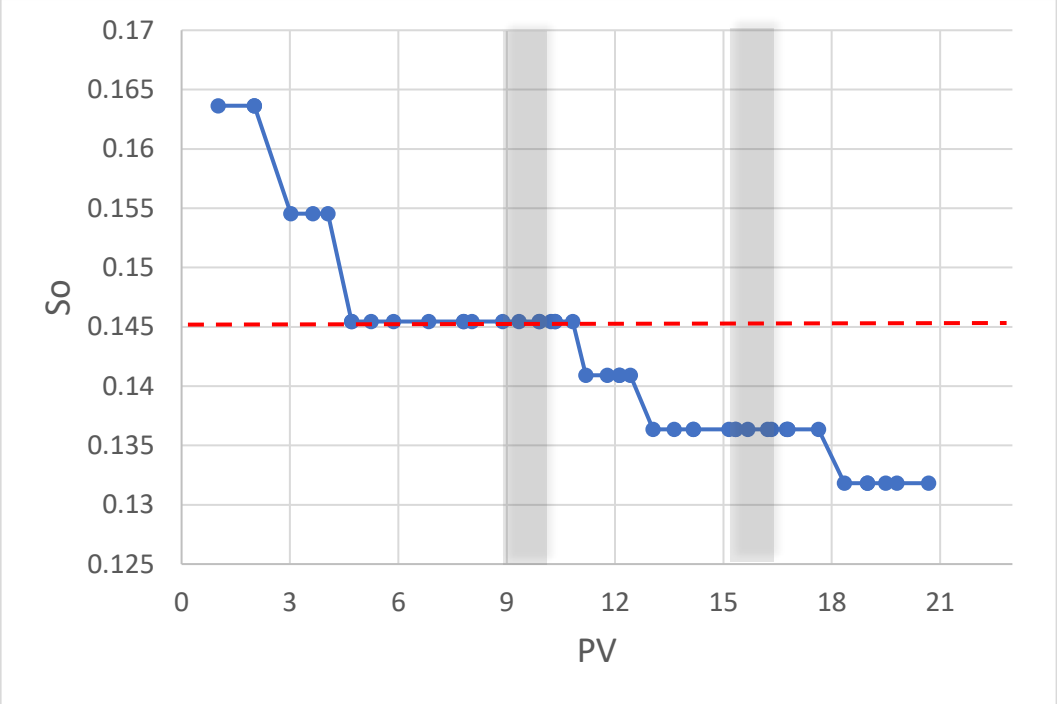

Figure 3-5 Oil saturation vs non-gas agent for Ottawa sand + Middle East oil+15 wt.% ammonium hydroxide

In this work, there was no aging procedure adopted before initiating the flow-through test as described previously, so there were less dramatic wettability reversal phenomena detected in sandpacks due to the presence of polar components in the crude samples. As a result, the residual oil saturation levels were quite similar in both cases of pure n-dodecane and Middle East crude.

Based on the results from these four tests, the first 1 PV chemical slug injection has generated higher oil recovery. However, the second 1 PV chemical slug injection exhibits much less oil recovery. During the first urea or ammonium hydroxide injection process and flowing first shut-in period, the oil cut and in-situ surfactant generated more over first stage than second shut-in stage due to the large decrease of S_{or} at the beginning.

3.4.2 Indiana Limestone Tests

The in-situ CO_2 by using urea has proved the ability for improving the oil recovery in sandstone. An abundance of hydrocarbon deposits in the carbonate reservoir around the world, especially in the Middle East regions. The different rock properties between the carbonate rock and sandstone might have different effects during in-situ CO_2 EOR using urea. In this work, 4 flow-through tests were conducted by using Indiana limestone as a comparison group with Ottawa sand at the same conditions. Before the flow through test, the sample preparation followed same procedure for crushing and sieving to same mesh size. Moreover, there was no aging treatment to significantly affect initial wettability. Table 3-5 shows the test condition for Indianan limestone.

Test #	5	6	7	8
oil type Brine	Dodecane sea water	Dodecane sea water	Middle-East oil sea water	Middle-East oil sea water
Chemical concentration, %	35% Urea	15% Ammonium Hydroxide	35% Urea	15% Ammonium Hydroxide
T, °C	120	120	120	120
Back pressure, psi	1500	1500	1500	1500
Injection rate, ml/min	0.3	0.3	0.3	0.3
Sor	33.80%	25.60%	36.70%	28.06%

Table 3-5 Flow through column test condition for Indiana limestone

The experiments results were plotted by oil saturation against pore volumes of chemical slug and seawater injected. The test #5 was designed as a comparison test with test #1, using pure n-dodecane and 35wt% urea as gas generation agent and shows by Figure 3-

6. After injecting enough PVs seawater for pre-flooding, the Sor was 33.84%. And then followed by 1 PV chemical slug and first 72 hours shut-in stage, the tertiary recovery was 5.68%.

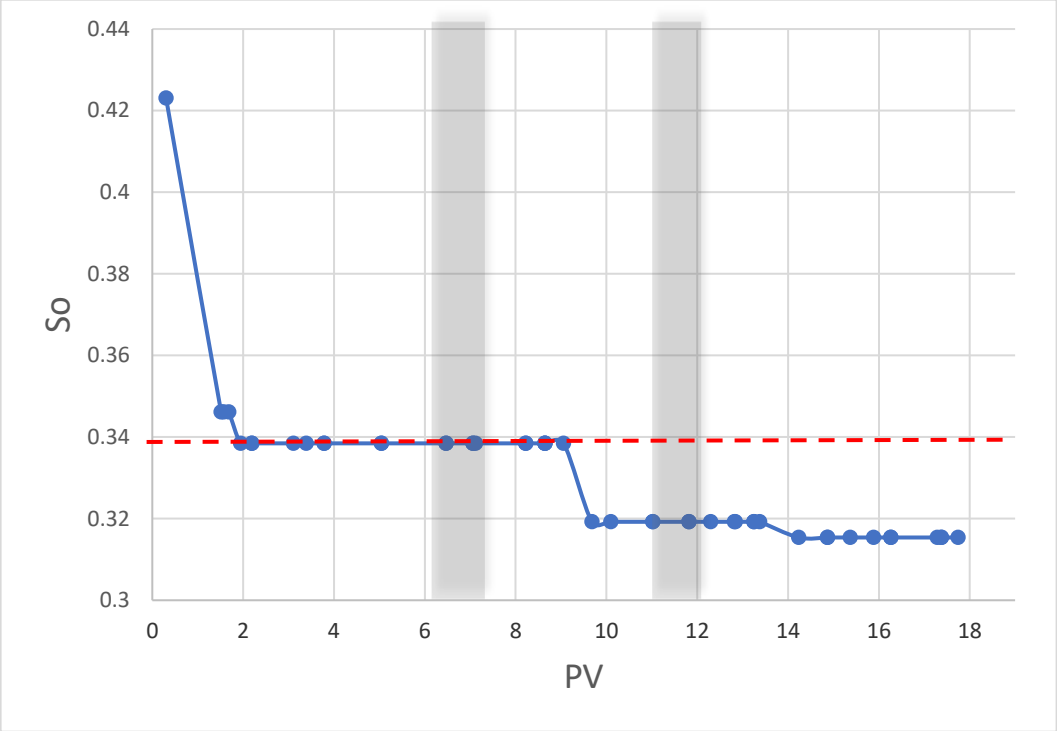

Figure 3-6 Oil saturation vs gas agent urea for Indiana limestone+Dodecane+35 wt.% Urea

Next, the second stage of chemical slug injection and shut-in cycle achieved tertiary recovery 1.13%, so the final Etr achieved was 6.81%.

In test #6, in order to isolate CO_2 effects by gas generation agent, the non-gas agent 15. wt% ammonium hydroxide was used with pure-n alkane dodecane. After reached Sor

25.6%, the two stages of chemical slug injection and shut-in cycles both had negligible tertiary recovery as indicated by Figure 3-7.

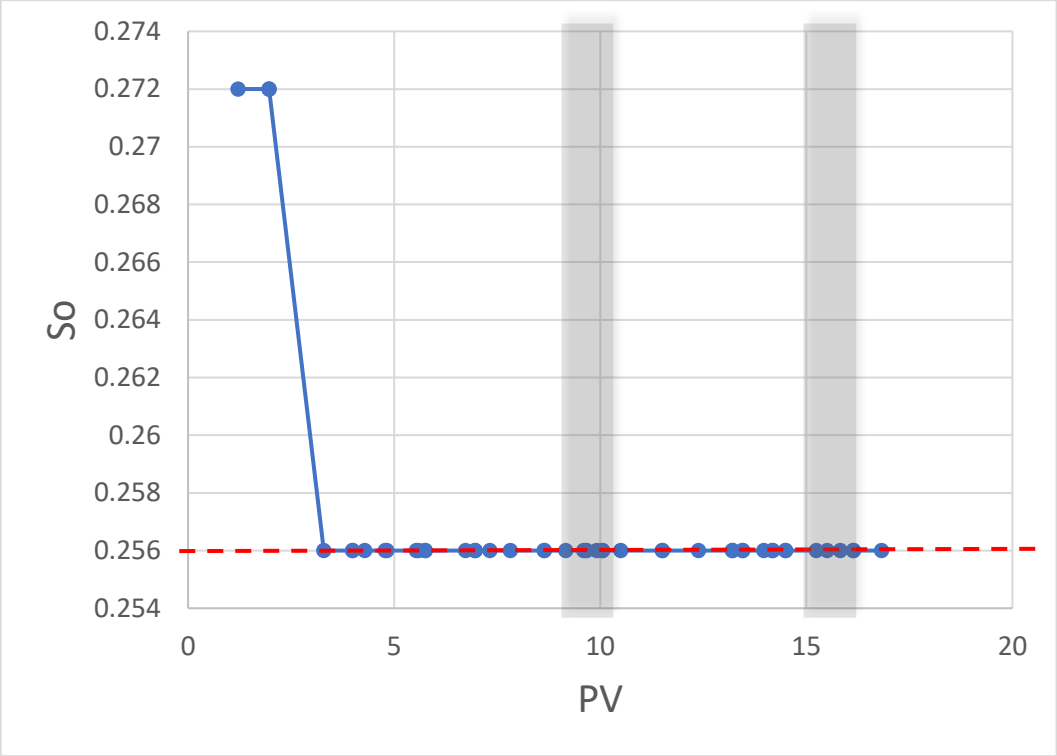

Figure 3-7 Oil saturation vs non-gas agent for Indiana limestone+Dodecane+15 wt.% ammonium hydroxide

There was no oil production observed after shut-in cycles, which significantly differed from sandstone condition (5.17% Etr). Without CO_2 gas transfer and polar components in crude oil, the Etr was dominated by wettability effect.

Test #7 combined the effects of CO_2 and polar components in crude with gas agent urea. Figure 3-8 represents the oil saturation decreases by chemical slugs and seawater injection. Once approached Sor 36.71%, the first tertiary recovery of urea slug injection

and shut-in was 10.47% and the second tertiary recovery was 1.9%. Therefore, the total final Etr was 12.37%.

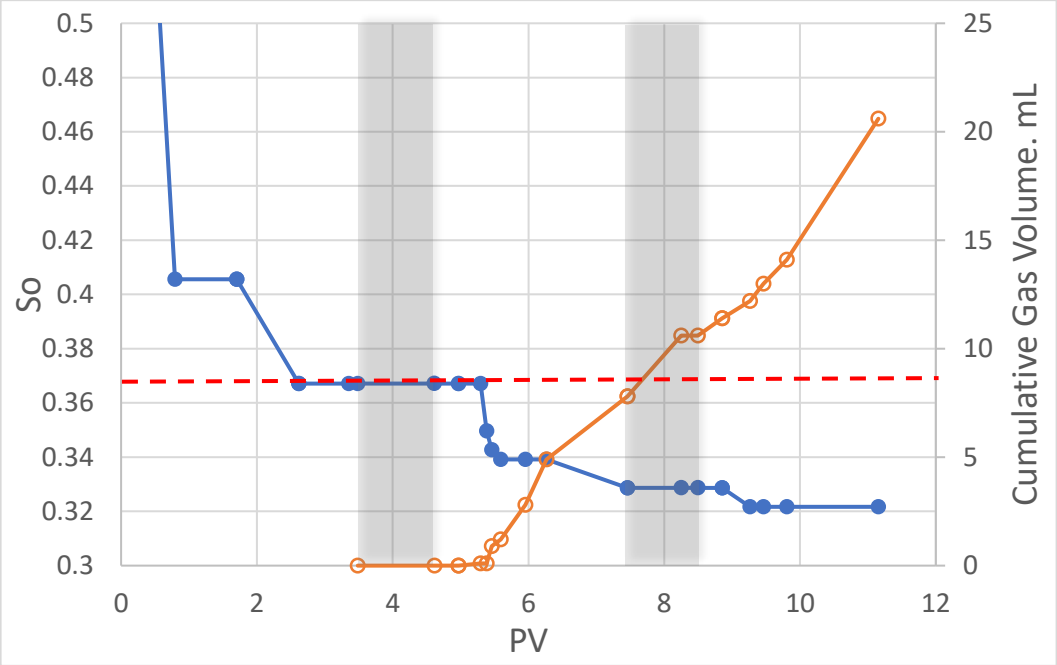

Figure 3-8 Oil saturation vs gas agent for Indiana limestone+Middle East oil+35 wt.% urea

It can be seen from the orange line, which indicates cumulative CO_2 gas volume collection. When urea started to generate CO_2, the oil saturation dropped. As we can see, after first stage of urea slug injection, the oil saturation decreased greater than second stage, but the amounts of CO_2 generated are quite similar during the first and second stages. This was because most of the trapped oil were released during the first stage injection, and the new low oil saturation in the media therefore resulted in lower

oil cut during second chemical slug injection stage while the amount of CO2 generated remains about the same.

The last test #8 isolated CO_2 effects by using 15 wt.% ammonium hydroxide. The polar components in crude oil reacting with ammonium hydroxide would affect the net oil production. Figure 3-9 represents the Sor as 28.06%, and after first chemical slug injection and shut-in period, the tertiary recovery was 2.81%.

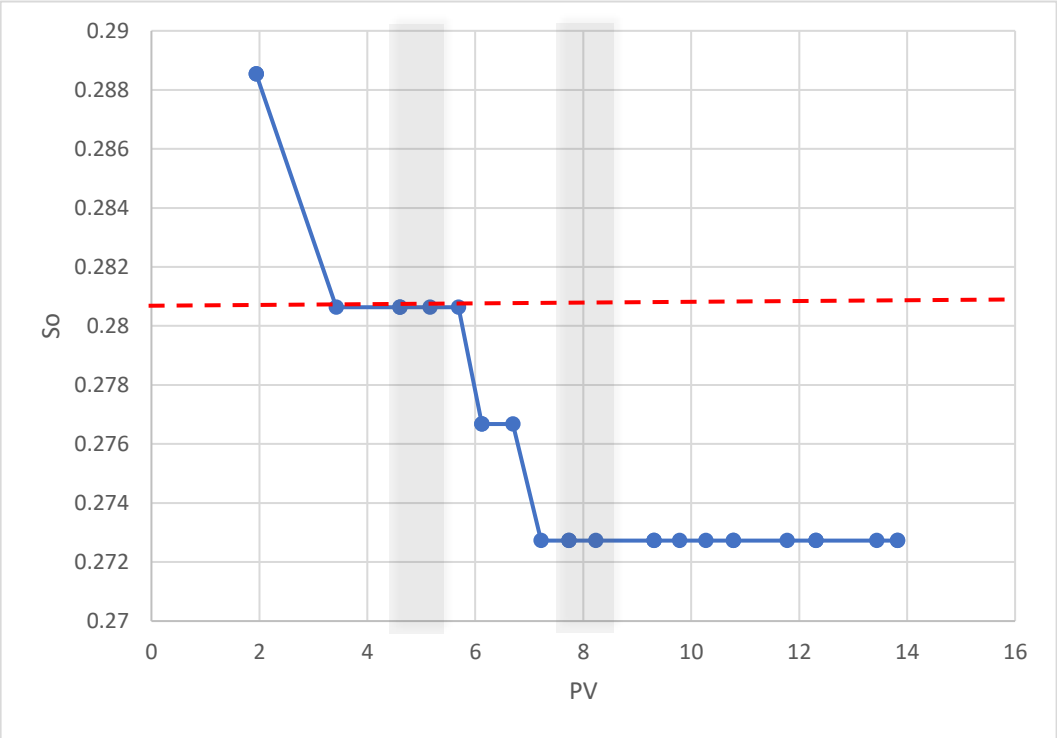

Figure 3-9 Oil saturation vs non-gas agent for Indiana limestone + Middle East oil + 15 wt.% ammonium hydroxide

In this case, most of the oil produced during the first stage, as a result, after second chemical slug injection and shut-in treatment, there was no more entrapped oil could be

extracted. Therefore, the second tertiary recovery was negligible. The final tertiary recovery was accounted mainly due to the first stage of Etr, 2.81%.

3.4.3 Silurian Dolomite Tests

Another type of carbonate rock Silurian Dolomite was used in this work. The basic chemical composition of Indiana limestone is calcium carbonate ($CaCO_3$). However, the Silurian dolomite contains magnesium $CaMg(CO_3)_2$ in the mineral composition. According to literatures review, the presence of magnesium ions could alter the wetting properties of carbonate rocks. So, it was predicted that the performance of the tertiary recovery in Silurian dolomite would be between the Indiana limestone and Ottawa sand. Because of the limitation of experiment period, each single test would take one week, there were two tests conducted for Silurian dolomite. Table 3-6 represents the test condition.

Test #	9	10
oil type	Middle-East oil	Middle-East oil
Brine	sea water	sea water
chemical concentration, %	35% Urea	35% Urea
T, ^oC	120	120
Back pressure, psi	1500	1500
Injection rate, ml/min	0.3	0.3
Sor	28.69%	31.30%

Table 3-6 Flow through column test condition for Silurian dolomite

The optimum test condition using crude oil with gas agent urea, had highest tertiary recovery 26.97% and 12.37% in sandstone and limestone, respectively. So, test #9 was

a comparison test with Silurian dolomite under the same optimum condition and was shown by Figure 3-10.

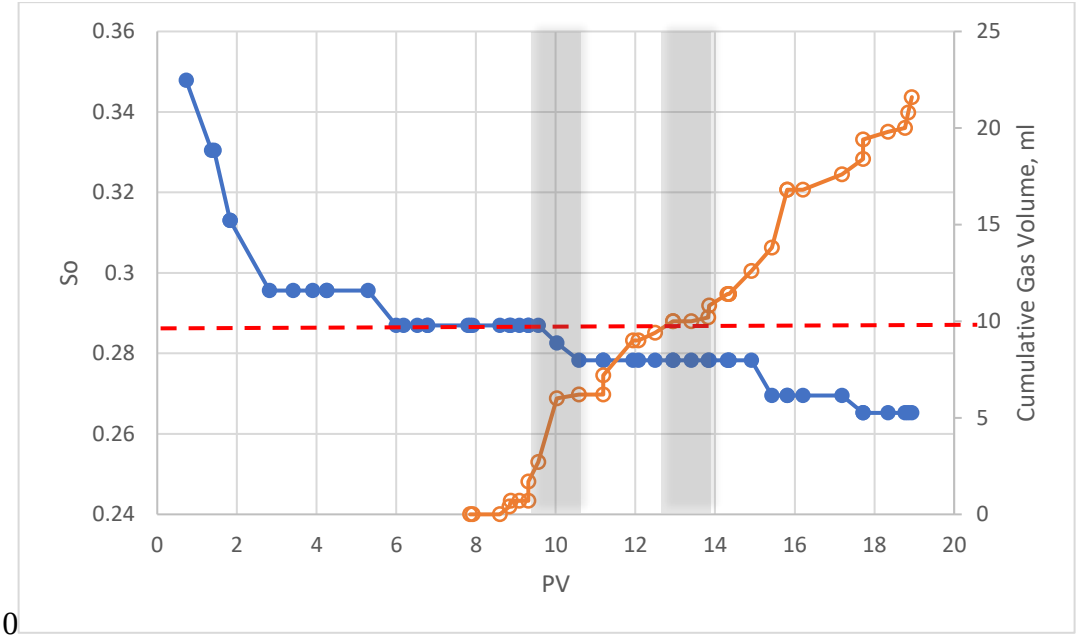

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Figure 3-10 Oil saturation vs gas agent for Silurian dolomite + Middle East oil + 35 wt.% Urea

The residual oil saturation was 28.69% after adequate seawater pre-flooding, and then followed by 2 PVs urea slug injection and shut-in treatment, the first tertiary recovery was 3.03% and second tertiary recovery was 4.54%. Thus, the total tertiary recovery was 7.57%. The Etr was lower than Indiana limestone Etr of 12.37%, which was against our original prediction. Test #10 was carried out to repeat test #9 confirm the result in Test 9. The same test condition and procedure were followed, and Figure 3-11 indicates

the repeatable result. The similar value of Sor was observed, which was 28.26%.

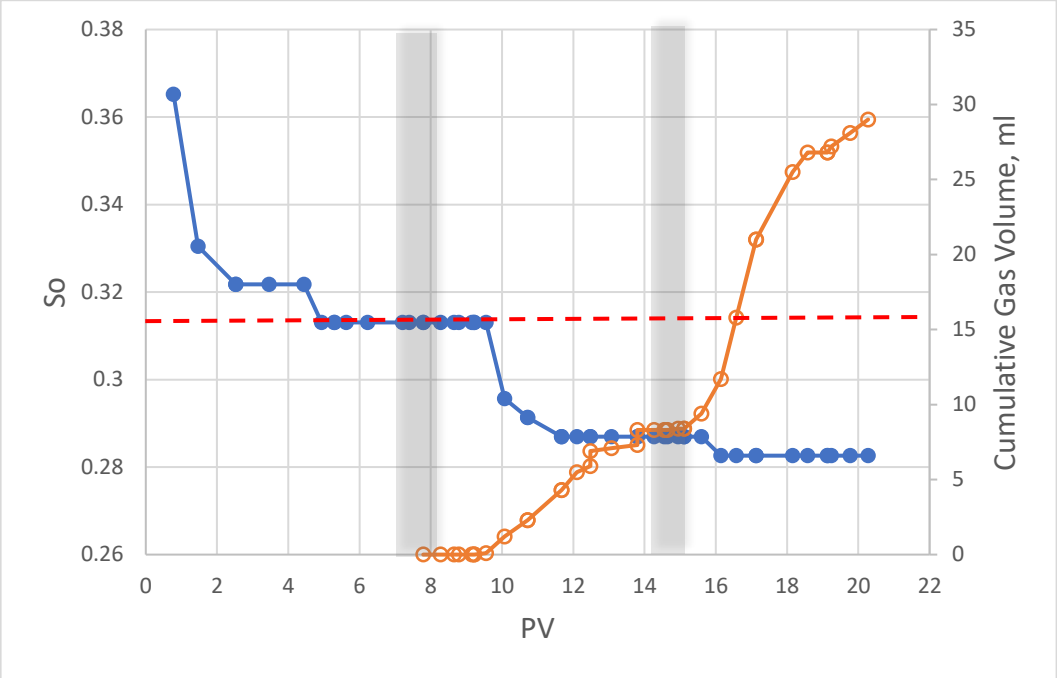

Figure 3-11 Oil saturation vs gas agent for Silurian dolomite + Middle East oil + 35 wt.% Urea repeat test

And the first and second urea tertiary recovery was 8.33% and 1.39%, respectively. Therefore, the total final tertiary recovery was 9.72%, which was slightly higher than test #9 Etr of 7.57%. The results of Etr on both test #9 and #10 were lower than that of Indiana limestone Etr 12.37% under same test condition. Consequently, the performance of the tertiary recovery by using gas agent urea exhibited the highest efficacy in sandstone media, modest level with limestone and the lowest case in dolomite.

3.4.4 Additional Indiana limestone Tests

Acid number (AN) is an important factor in crude oil, which can affect the oil recovery by alkali flooding. Because of the complex chemical composition in crude oil, the acidic components, such as long chain carboxylic acid group can react with alkaline solution and generate in-situ surfactant. This in-situ surfactant can lower the interfacial tension between the oil and water for improving the oil recovery. Therefore, the higher acid number of the crude oil with lower interfacial tension will result a better performance in EOR. There were two types of crude oil used in this test, the properties of the crude are summarized in Table 3-7.

	Middle East oil	Earlsboro oil
API	38	40
μ, cp	2.1	4.6
Density g/ml	0.834	0.825
Acid Number	relative low	relative high

Table 3-7 Oil properties for Middle East crude oil and Earlsboro crude oil

As we can see from the table, both crude oil has similar properties. However, Earlsboro crude should have a relatively higher acid number than Middle East crude oil, which was inferred from IFT measurement in Chapter 2. So Earlsboro oil with a lower IFT should form more in-situ surfactant than Middle East oil. The Indiana limestone was filled with these two types of oil by using non-gas agent 15 wt.% ammonium hydroxide as comparison tests. Figure 3-12 represents the result of test #11. The Sor was 51.44%, which was higher than test #8. As a result, the amount of trapped oil was much higher than test #8. The tertiary recovery was 9.6% and 5.6% after first and second chemical

slug injection, respectively. So, the final total tertiary recovery

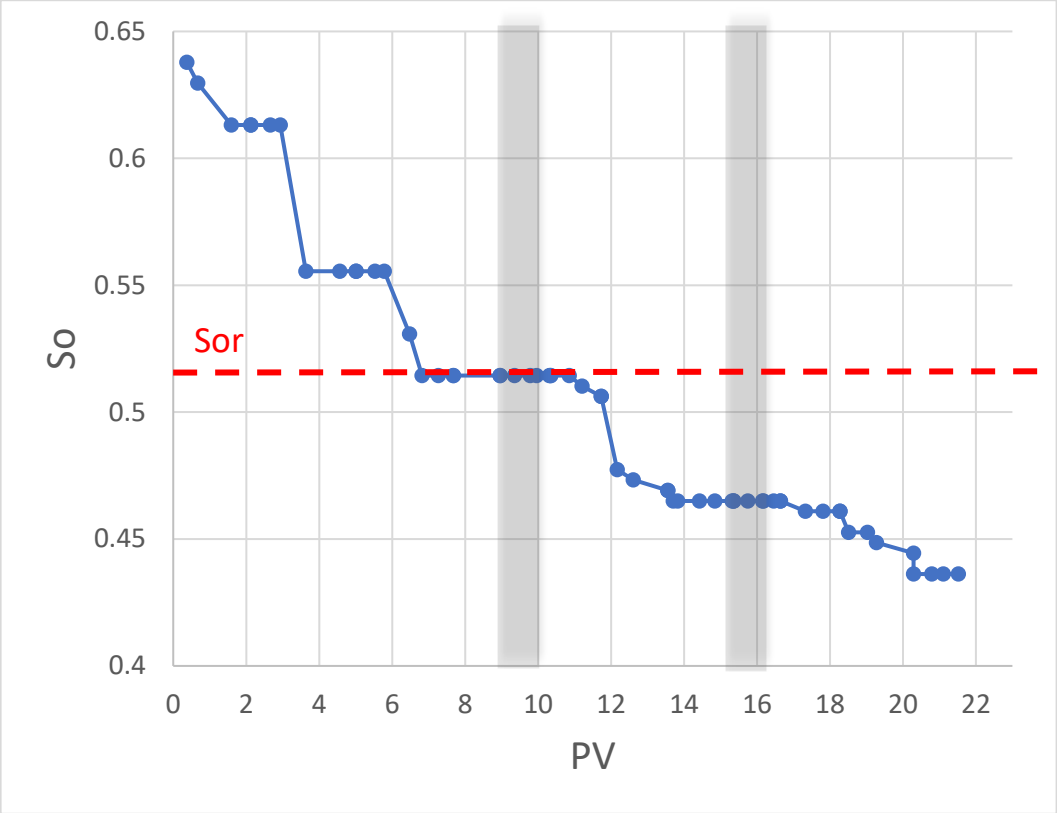

Figure 3-12 Oil saturation vs non-gas agent for Indiana limestone + Earlsboro oil + 15 wt.% ammonium hydroxide

was 15.2%, which was significantly higher than test #8 Etr 2.81%. There were two plausible reasons for such high Etr. Firstly, the higher Sor and correspondingly more trapped crude oil left after primary seawater flooding. During the two stages of chemical slug injection, more trapped oil could be extracted from porous media. Each single steel column test was tried to be consistent during the packing process, but it may still exist some human errors. Based on these tests result, the Sor was varying from 25.6% to 51.44% for Indiana limestone. Secondly, the relatively higher acid number of

Earlsboro oil was capable to generate more in-situ surfactant with produced ammonium hydroxide. Previously in Chapter 2, we discussed IFT measurement result between crude and alkaline solution. In short, the large reduction of IFT between aqueous phase and trapped oil hence results in better oil recovery.

In this work, eight flow-through tests were laid out in Figure 3-13. The blue bar represents residual oil saturation (Sor) and orange bar represents the tertiary recovery (Etr). The original wettability of sandstone was most likely water-wet, on the contrary the limestone was neutral to oil wet. Moreover, larger amount of

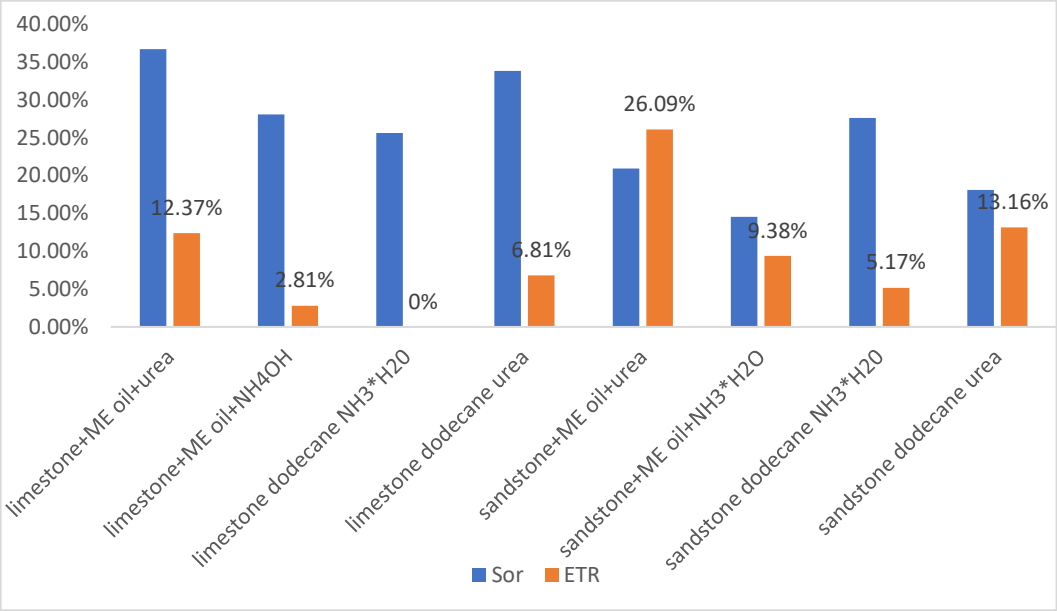

Figure 3-13 Eight flow through tests for Sor and ETR on sandstone and limestone

oil was produced by seawater pre-flooding before reaching the Sor in sandstone tests. As a result, all four sandstone tests had relatively lower Sor than limestone. The value

of Sor varied from 14.54% to 27.62% for sandstone while from 25.60% to 36.71% for limestone.

The three predominant mechanisms for improving tertiary recovery in this work include CO_2 resulted oil swelling, surfactant generation and wettability reversal. The gas generating urea decomposed to CO_2 and NH_3 at elevated temperature. Most of the CO_2 gas dissolved into aqueous phase. Because of a higher solubility of CO_2 in crude oil, the dissolved CO_2 in seawater would readily migrate into the crude oil phase, which caused oil swelling and oil viscosity reduction. Figure 3-14 indicates the cumulative CO_2 gas volume collection for three different types of rock.

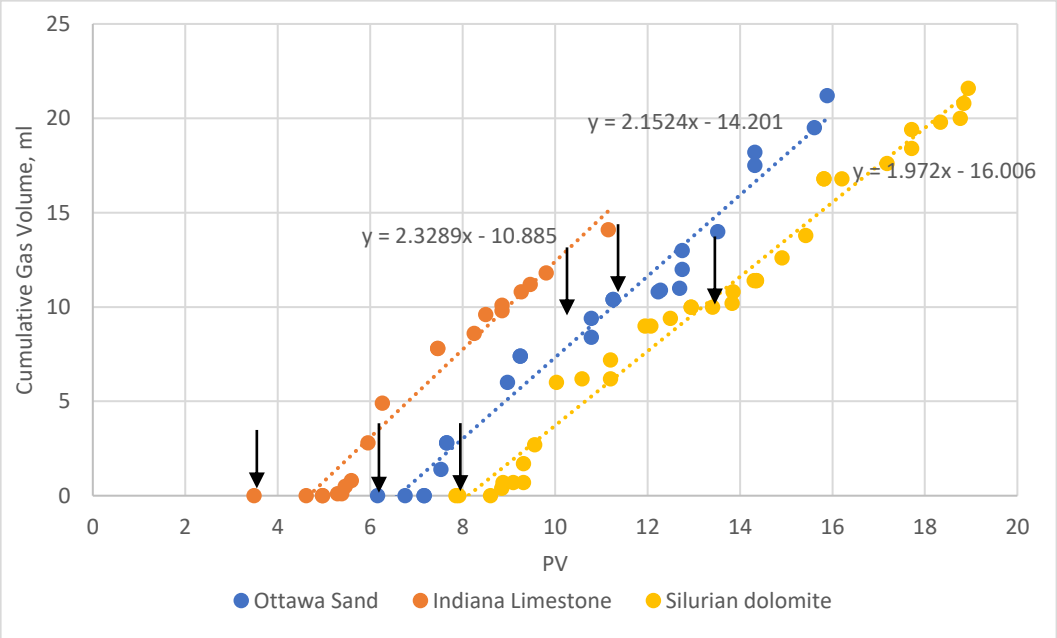

Figure 3-14 Cumulative in-situ CO_2 gas volume collection for three types of rock by consistent gas collection system

The arrows represent the two stages of urea slug injection. The method for CO_2 gas collection in this work was water replacement, in order to get consistent gas volume, it is necessary to avoid any leaking issue during the gas collection parts. From the Figure 3-14, after injecting each urea slug, the cumulative CO_2 gas volume has similar slope, which means similar amount of the CO_2 produced in each stage. However, for Indiana limestone column test, it has a little bit of higher slope than others indicating slightly higher CO_2 gas volume. This experiment error is acceptable.

The CO_2 will cause the oil swelling and then reduce the oil viscosity, as a result, more mobile crude can be easily produced. Apart from CO2, the urea will also provide ammonium hydroxide during the high temperature decomposition process. The individual effect of ammonium hydroxide was systematically studied. Figure 3-15 shows the comparison in tertiary recovery by using urea and ammonium hydroxide in sandstone and limestone.

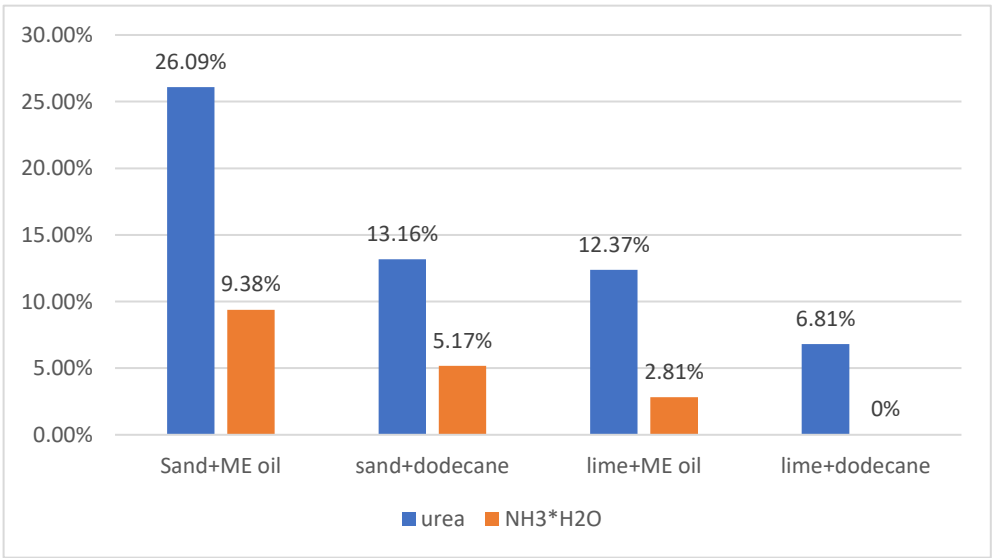

Figure 3-15 CO_2 effects for Etr in Ottawa Sand and Indiana Limestone

The blue bar represents urea slug injection and orange bar was ammonium hydroxide injection. All these four pairs column tests had significant higher tertiary recovery by using urea than ammonium hydroxide because of CO_2 generation. The tertiary recovery by using CWI and in-situ CO_2 generation method from other literature tests were summarized in Table 3-8. The highest tertiary recovery in this work was 26.09% for Ottawa sand in Middle East oil with 35% urea. Comparing this work with literature tests which has similar tertiary recovery when CO_2 presents in both crude and pure-n alkane oil.

Author	Mosavat and Torabi [14]	Fathollahi and Rostami [46]	Wang et al. [42]	Alam and Mahmoud [46]	Wang et al. [21]
Rock Type	Sand (99.88% SiO2)	Core (Calcite, dolomite and quartz)	Ottawa Sand	Indiana Limestone	F-95 Ottawa sand
Oil API	45.4	Decane	40	30	40
Oil viscosity, cp	2.76	Decane	4.6		4.6
Back pressure, psi	594-1494	2000	1500	1000	1500
Gas generation agent	CO2, CWI	CO2, CWI	urea	citric acid	Ammonium Carbamate
Concentration, %			35%	2-10%	35
Temp, °F	104	84	250	210	250
Etr, %	16.5-33.5%	8.4	35.85	3.94-27.95%	31.19

Table 3-8 Literature reported CWI and in-situ CO2 generation experiments

Another two important mechanisms for EOR in this work are surfactant generation by alkaline solution interacting with crude oil and wettability alteration of rock surface. The pure-n alkane dodecane do not contains any polar components like organic acids. Based on the results of IFT measurement reported in Chapter 2, the in-situ surfactants are generated when the crude oil with carboxylic acid reacts with alkali. Meanwhile, the generated in-situ surfactant forms water-oil emulsion, which is entrapped in the pore media. This emulsion can lower the water injection mobility and then increase the sweep efficiency. Figure 3-16 represents the effect of in-situ surfactant generation for EOR in two types of oil.

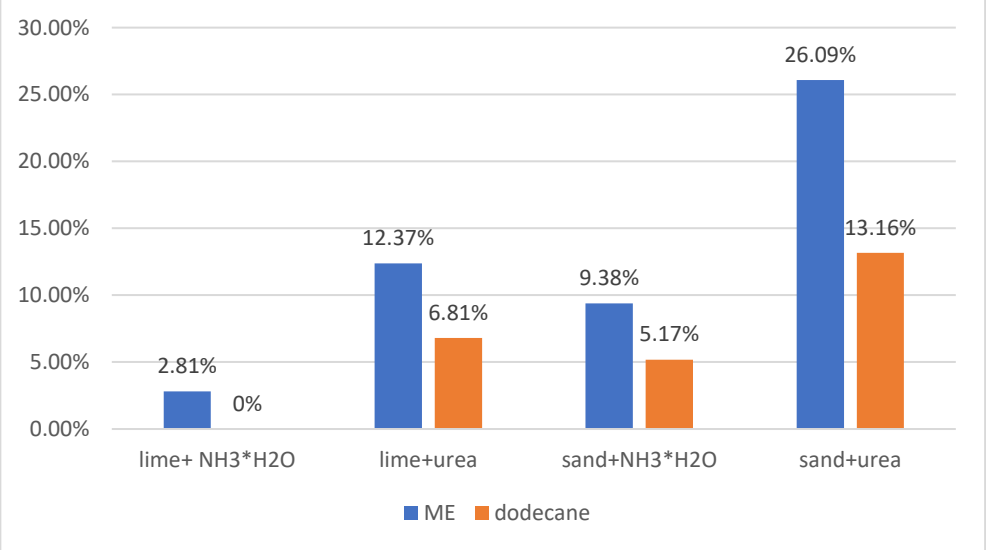

Figure 3-16 Effects of surfactant generation for Etr in Middle East oil and Dodecane with alkaline solution

The Middle East oil represented by blue bar has greater tertiary recovery than dodecane. The optimum case Ottawa sand with urea in crude oil has the highest Etr, 26.09%, while

Indiana limestone with urea and dodecane has around half value of Etr, 12.37%. Moreover, without CO_2 effects by urea decomposition and surfactant generation from crude oil, the Indiana limestone with ammonium hydroxide and dodecane has 0 oil cut during the test. Whereas, the same condition for Ottawa sand has 5.17% Etr. So, the wettability of the rock surface plays an important role. The silica sand surface has negative charge and mostly water-wet. After pre-flooding process, it will reach relative lower residual oil saturation than limestone. Also, during the seawater flooding, the seawater could not liberate largely bitumen and asphaltenes which adsorbed on the sand surface. However, the ammonia produced from the urea has ability to largely release those polar components and reverse the sand surface to more water-wet. In addition, the carbonate surface has positive charge, and the negative charge of carboxylic material in the crude oil will form strong bonds to the positive charge carbonate surface. Therefore, the water-wet is sharply decreasing as increasing the amount of carboxylic material in crude oil. Moreover, the common divalent ions in the seawater could provide potential wettability alteration. The divalent ions calcium, magnesium and sulfate in the seawater contain opposite charge; these divalent ions can adsorb onto the carbonate surface. Because of the positive charge surface of carbonate, the SO_4^{2-} will adsorb onto the surface and decrease the positive charge density. Then the adsorption of Ca^{2+} and Mg^{2+} on carboxylic material will increase, hence results in liberation of bitumen and asphaltenes. So, it is believed that those divalent ions could co-adsorb onto the carbonate surface for wettability alteration. Figure 3-17 indicates the effects of

wettability reversal for Etr.

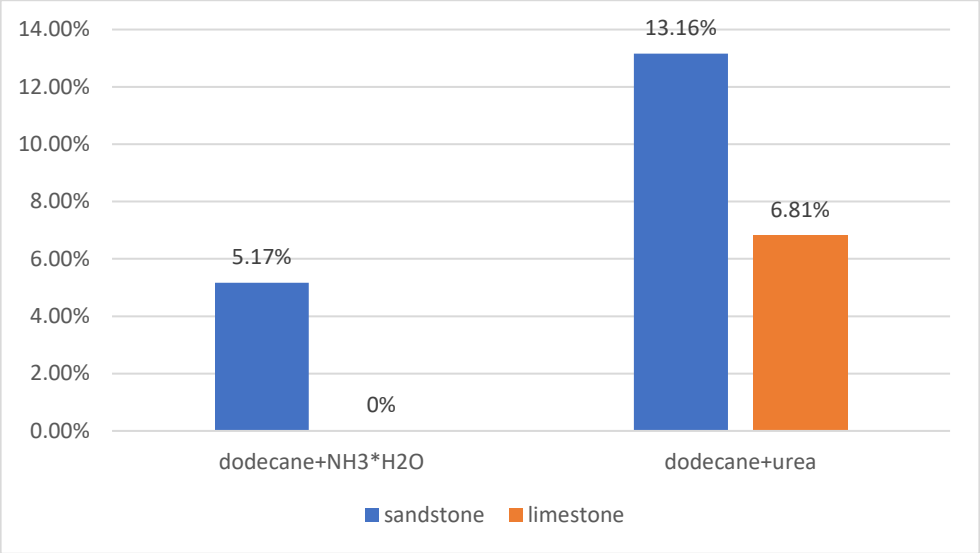

Figure 3-17 Effects of wettability reversal by divalent ions in seawater for Ottawa Sand and Indiana Limestone

To isolate surfactant generation effects, the pure-n alkane dodecane oil was used as comparison test. Because of low concentration of divalent ions in seawater, the wettability reversal did not significantly affect the tertiary recovery, for example, in limestone with ammonium hydroxide slug, it has 0 Etr. So, the divalent ions did not obviously cause wettability reversal in this work. The initial wettability of silica sand is water-wet, even without any surfactant and CO_2 effects, it still has 5.17% of Etr.

Around half of the proven oil reserve is present in the carbonate reservoir, so the dolomite rock is also an important reservoir rock. Silurian dolomite was used in this work, the composition of Silurian dolomite contains Mg^{2+}. Moreover, because of the positive charge of the dolomite surface, the carboxylic materials present in the crude oil

can easily adsorb onto its surface. Due to the presence of divalent ions in seawater and ammonia generation from urea, it is believed that the chemical reaction to release the carboxylic material in dolomite should have similar performance with limestone. Therefore, the same standard tests were carried out for Silurian dolomite. The Figure 3-18 indicates the optimum test condition by using urea and crude oil for tertiary recovery with three different types of rock.

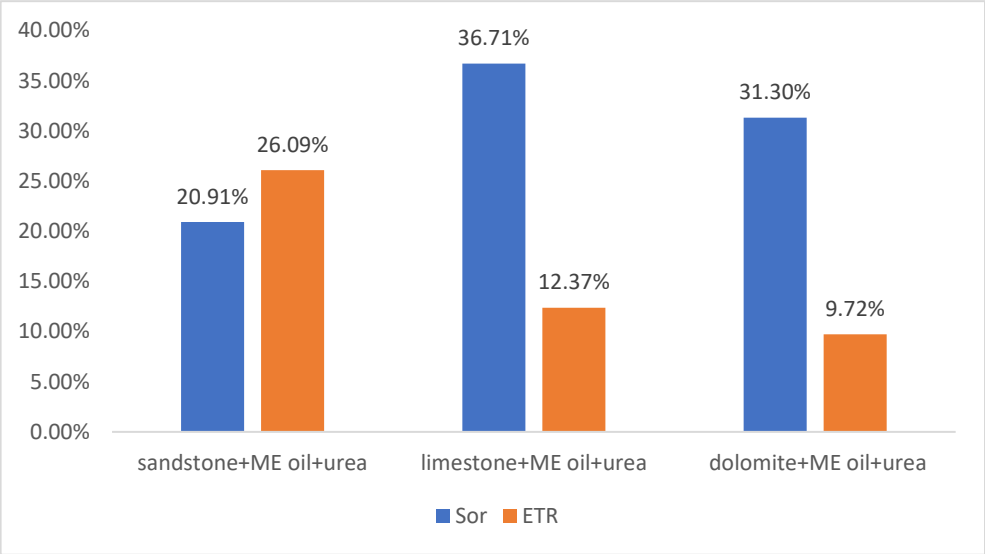

Figure 3-18 The changing in tertiary recovery for different types of rock by optimum test condition

The wettability can be indicated by Amott_Harvey wettability index (I_{A_H}). The range of oil wet is -1 to -0.3, -0.3 to 0.3 is neutral wet and 0.3 to 1 is water wet. The initial wettability of dolomite and limestone are oil-wet, after introducing seawater flooding, it causes both rocks to become more neutral-wet. however, the wettability index of dolomite rock will move up more toward the boundary between the neutral-wet and

water-wet zone [10]. As a result, the wettability reversal will be more obvious for dolomite. However, because of CO_2 generation by urea decomposition, the CO_2 will dissolve into seawater to form carbonate water. The wettability alteration by carbonated seawater injection in both rocks could turn the rock wettability from the oil-wet to neutral wet [10]. Table 3-9 shows Amott_Harvey wettability index measurement with seawater and carbonate seawater for both limestone and dolomite by Muñoz, Winter and Trevisan.

Amott_Harvey wettability index (I_{A_H})			
		Dolomite	Limestone
Seawater	Initial	-0.4583	-0.3915
	After	0.2821	0.0736
Carbonate seawater	Initial	-0.4163	-0.1373
	After	-0.2154	0.2564

Table 3-9 Amott_Harvey wettability index (I_{A_H}) measurement [10]

Consequently, the wettability reversal observed for dolomite by injecting carbonated seawater is less marked than limestone. The CO_2 dissolved in seawater inhibits wettability of dolomite turning to neutral-wet and water-wet situation. So, from the Figure 3-18, the Silurian dolomite has the lowest tertiary recovery 9.72%, the Indiana limestone meets the medium Etr 12.37% and Ottawa sand has the highest tertiary recovery 26.09% under the same test condition.

The additional tests for two different types of crude oil Middle East oil and Earlsboro oil aimed to prove different acidic crude affect EOR by surfactant generation. According to the IFT measurement result from Chapter two, the Earlsboro oil has lower interfacial tension than Middle East oil against alkaline solution. So, from what has

been discussed before, we can draw the conclusion that Earlsboro oil has relatively higher acid number than Middle East oil. The Figure 3-19 shows the flow-through test for tertiary recovery by using these two types of crude oil.

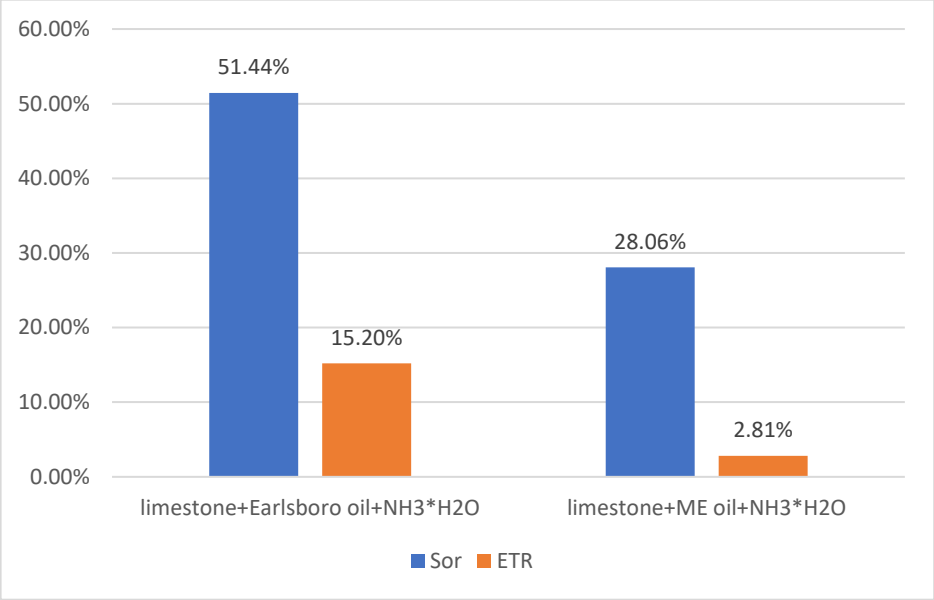

Figure 3-19 Effect of relatively higher Acid Number of Earlsboro oil and lower Acid Number Middle East oil for tertiary recovery by surfactant generation

The Indiana limestone was used for this comparison test with alkaline solution ammonium hydroxide and Earlsboro oil; it leads more than 5 times higher tertiary recovery than Middle East oil. It is not only because of the higher residual oil saturation reached but also owing to more in-situ surfactant generated from relatively higher acid number Earlsboro oil.

The Table 3-10 summarizes tertiary recovery for all 11 tests in this work. It is encouraging that Ottawa sand tests lead greater enhancement of tertiary oil recovery

than Indiana limestone and Silurian dolomite by in-situ CO_2 generation system. And the first 1 PV chemical slug injection contributes more to the final tertiary oil recovery than second 1 PV chemical slug injection. The average of total tertiary recovery is 13.44%, 5.5% and 8.64% for sandstone, limestone and dolomite, respectively.

	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11
Total Etr	13.15%	5.16%	26.08%	9.38%	6.81%	0.00%	12.37%	2.81%	9.72%	7.57%	15.20%
1st PV Etr	7.89%	3.44%	17.39%	6.25%	5.68%	0%	10.47%	2.81%	8.33%	4.54%	9.60%
2nd PV Etr	5.26%	1.72%	8.69%	3.13%	1.13%	0%	1.90%	0%	1.39%	3.03%	5.60%

Table 3-10 Summary of tertiary recovery for all 11 tests

Chapter 4: Conclusions and Recommendations

4.1 Conclusions and recommendation

The in-situ CO_2 EOR technology can eliminate the adverse effects of conventional CO_2-EOR. After running several flow-through experiments, the optimum tertiary recovery for both sandstone and carbonate rock was achieved by using 35% concentration of urea with light crude oil at high pressure and high temperature condition. It has proven that urea, as an in-situ gas generation agent, can significantly increase tertiary recovery for sandstone than carbonate rock. The main mechanisms of in-situ CO_2 EOR by using urea include oil swelling, viscosity reduction, IFT dropping by increasing in alkalinity, and wettability alteration. Moreover, running experiments below the minimum miscible pressure (MMP) at 1500 psi backup pressure show the same benefits observed in miscible flooding. On the other hand, comparing with alkali/surfactant/polymer (ASP) complex system, the single chemical used in-situ CO_2 generation system is much simpler and economically feasible.

Because of the long period of each single flow-through test, there were only two tests conducted for dolomite in optimum condition. In future work of this in-situ CO_2 study, it is recommended to complete comprehensive tests in dolomite, which will better prove the benefit of tertiary recovery in different rocks. Also, this research only focuses on conventional reservoir, the in-situ CO_2 EOR system could be a promising technology for unconventional shale reservoir as well. Moreover, light oil with API around 40 was

tested in the experiments. The future study is recommended to examine the performance of in-situ CO_2 EOR with various heavy oils in different rock formations.

Reference

1. Conti, J. J.; Holtberg, P. D.; Beamon, J. A.; Schaal, A. M.; Ayoub, J.; Turnure, J. T., Annual energy outlook 2018. *US Energy Information Administration* **2018**.

2. Alvarado, V.; Manrique, E., Enhanced Oil Recovery: An Update Review. *Energies* **2010,** *3*, (9), 1529-1575.

3. Rubin, E.; De Coninck, H., IPCC special report on carbon dioxide capture and storage. *UK: Cambridge University Press. TNO (2004): Cost Curves for CO2 Storage, Part* **2005,** *2*.

4. Wang, X.; Yuan, Q.; Wang, S.; Zeng, F. In *The First Integrated Approach for CO 2 Capture and Enhanced Oil Recovery in China*, Carbon Management Technology Conference, 2017; Carbon Management Technology Conference: 2017.

5. Verma, M. K., Fundamentals of carbon dioxide-enhanced oil recovery (CO₂-EOR): a supporting document of the assessment methodology for hydrocarbon recovery using CO₂-EOR associated with carbon sequestration. **2015**.

6. Melzer, L. S., Carbon dioxide enhanced oil recovery (CO2 EOR): Factors involved in adding carbon capture, utilization and storage (CCUS) to enhanced oil recovery. *Center for Climate and Energy Solutions* **2012**.

7. Hawez, H.; Ahmed, Z., Enhanced oil recovery by CO2 injection in carbonate reservoirs. **2014,** *1*, 547-558.

8. Wang, S.; Chen, C.; Shiau, B.; Harwell, J. H., In-situ CO 2 generation for EOR by using urea as a gas generation agent. *Fuel* **2018,** *217*, 499-507.

9. Han, L.; Gu, Y., Optimization of Miscible CO2 Water-Alternating-Gas Injection in the Bakken Formation. *Energy & Fuels* **2014,** *28*, (11), 6811-6819.

10. Muñoz, E. R.; Winter, A.; Trevisan, O. V. In *Wettability Alteration in Limestone and Dolomite With Brines and CO2*, ASME 2015 34th International

Conference on Ocean, Offshore and Arctic Engineering, 2015; American Society of Mechanical Engineers: 2015; pp V010T11A026-V010T11A026.

11. Lei, H.; Yang, S.; Zu, L.; Wang, Z.; Li, Y., Oil Recovery Performance and CO2 Storage Potential of CO2 Water-Alternating-Gas Injection after Continuous CO2 Injection in a Multilayer Formation. *Energy & Fuels* **2016,** *30*, (11), 8922-8931.

12. Dong, Y.; Dindoruk, B.; Ishizawa, C.; Lewis, E. J. In *An experimental investigation of carbonated water flooding*, SPE Annual Technical Conference and Exhibition, 2011; Society of Petroleum Engineers: 2011.

13. Sohrabi, M.; Riazi, M.; Jamiolahmady, M.; Idah Kechut, N.; Ireland, S.; Robertson, G., Carbonated water injection (CWI)–A productive way of using CO2 for oil recovery and CO2 storage. *Energy Procedia* **2011,** *4*, 2192-2199.

14. Mosavat, N.; Torabi, F., Performance of Secondary Carbonated Water Injection in Light Oil Systems. *Industrial & Engineering Chemistry Research* **2013,** *53*, (3), 1262-1273.

15. Simon, R.; Graue, D., Generalized correlations for predicting solubility, swelling and viscosity behavior of CO2-crude oil systems. *Journal of Petroleum Technology* **1965,** *17*, (01), 102-106.

16. Duan, Z.; Sun, R.; Zhu, C.; Chou, I. M., An improved model for the calculation of CO2 solubility in aqueous solutions containing Na+, K+, Ca2+, Mg2+, Cl−, and SO42−. *Marine Chemistry* **2006,** *98*, (2-4), 131-139.

17. Bakhtiyarov, S. *Technology on in-situ gas generation to recover residual oil reserves*; New Mexico Institute of Mining and Technology, 2008.

18. Gumersky, K.; Dzhafarov, I.; Shakhverdiev, A. K.; Mamedov, Y. G. In *In-situ generation of carbon dioxide: New way to increase oil recovery*, SPE European Petroleum Conference, 2000; Society of Petroleum Engineers: 2000.

19. Wang, Y.; Hou, J.; Tang, Y., In-situ CO2 generation huff-n-puff for enhanced oil recovery: Laboratory experiments and numerical simulations. *Journal of Petroleum Science and Engineering* **2016,** *145*, 183-193.

20. Bakhtiyarov, S. I.; Shakhverdiev, A. K.; Panakhov, G. M.; Abbasov, E. M.; Siginer, D. In *In-Situ Carbon Dioxide Generation for Oil Recovery: Experimental Study of Pressure and Temperature Variations During Stoichiometric Reaction*, ASME 2006 International Mechanical Engineering Congress and Exposition, 2006; American Society of Mechanical Engineers: 2006; pp 895-898.

21. Wang, S.; Kadhum, M. J.; Chen, C.; Shiau, B.; Harwell, J. H., Development of in Situ CO2 Generation Formulations for Enhanced Oil Recovery. *Energy & Fuels* **2017,** *31*, (12), 13475-13486.

22. Sahu, J.; Mahalik, K.; Patwardhan, A.; Meikap, B., Equilibrium and kinetic studies on the hydrolysis of urea for ammonia generation in a semibatch reactor. *Industrial & Engineering Chemistry Research* **2008,** *47*, (14), 4689-4696.

23. Koebel, M.; Strutz, E. O., Thermal and hydrolytic decomposition of urea for automotive selective catalytic reduction systems: thermochemical and practical aspects. *Industrial & engineering chemistry research* **2003,** *42*, (10), 2093-2100.

24. Southwick, J. G.; van den Pol, E.; van Rijn, C. H.; van Batenburg, D. W.; Boersma, D.; Svec, Y.; Anis Mastan, A.; Shahin, G.; Raney, K., Ammonia as alkali for alkaline/surfactant/polymer floods. *SPE Journal* **2016,** *21*, (01), 10-21.

25. Sheng, J. J., Investigation of alkaline–crude oil reaction. *Petroleum* **2015,** *1*, (1), 31-39.

26. Jeff, R.; Wasan, D. T., Surfactant-enhanced alkaline flooding: Buffering at intermediate alkaline pH. *SPE reservoir engineering* **1993,** *8*, (04), 275-280.

27. Flury, C.; Afacan, A.; Tamiz Bakhtiari, M.; Sjoblom, J.; Xu, Z., Effect of Caustic Type on Bitumen Extraction from Canadian Oil Sands. *Energy & Fuels* **2013,** *28*, (1), 431-438.

28. Samanta, A.; Ojha, K.; Mandal, A., Interactions between Acidic Crude Oil and Alkali and Their Effects on Enhanced Oil Recovery. *Energy & Fuels* **2011,** *25*, (4), 1642-1649.

29. Liu, Q.; Dong, M.-Z.; Asghari, K.; Tu, Y., Wettability alteration by magnesium ion binding in heavy oil/brine/chemical/sand systems—analysis of hydration forces. *Natural Science* **2010,** *02*, (05), 450-456.

30. Wang, Y.; Xu, H.; Yu, W.; Bai, B.; Song, X.; Zhang, J., Surfactant induced reservoir wettability alteration: Recent theoretical and experimental advances in enhanced oil recovery. *Petroleum Science* **2011,** *8*, (4), 463-476.

31. Al-Maamari, R. S.; Buckley, J. S. In *Asphaltene precipitation and alteration of wetting: can wettability change during oil production?* SPE/DOE Improved Oil Recovery Symposium, 2000; Society of Petroleum Engineers: 2000.

32. Leslie Zhang, D.; Liu, S.; Puerto, M.; Miller, C. A.; Hirasaki, G. J., Wettability alteration and spontaneous imbibition in oil-wet carbonate formations. *Journal of Petroleum Science and Engineering* **2006,** *52*, (1-4), 213-226.

33. Fjelde, I.; Asen, S. M. In *Wettability alteration during water flooding and carbon dioxide flooding of reservoir chalk rocks*, SPE EUROPEC/EAGE Annual Conference and Exhibition, 2010; Society of Petroleum Engineers: 2010.

34. Muñoz, E. R.; Winter, A.; Trevisan, O. V. In *Wettability Alteration in Limestone and Dolomite With Brines and CO2*, ASME 2015 34th International Conference on Ocean, Offshore and Arctic Engineering, 2015; American Society of Mechanical Engineers: 2015; pp V010T11A026-V010T11A026.

35. Sharma, G.; Mohanty, K., Wettability alteration in high-temperature and high-salinity carbonate reservoirs. *SPE Journal* **2013,** *18*, (04), 646-655.

36. Shariatpanahi, S. F.; Hopkins, P.; Aksulu, H.; Strand, S.; Puntervold, T.; Austad, T., Water Based EOR by Wettability Alteration in Dolomite. *Energy & Fuels* **2016,** *30*, (1), 180-187.

37. Shen, T.; Moghanloo, R. G.; Tian, W. In *Ultimate CO 2 storage capacity of an over-pressurized 2D aquifer model*, EUROPEC 2015, 2015; Society of Petroleum Engineers: 2015.

38. DiPietro, J. P.; Kuuskraa, V.; Malone, T., Taking CO2 Enhanced Oil Recovery to the Offshore Gulf of Mexico: A Screening-Level Assessment of the Technically and Economically-Recoverable Resource. *SPE Economics & Management* **2015,** *7*, (01), 3-9.

39. Sohrabi, M.; Kechut, N. I.; Riazi, M.; Jamiolahmady, M.; Ireland, S.; Robertson, G., Coreflooding studies to investigate the potential of carbonated water injection as an injection strategy for improved oil recovery and CO2 storage. *Transport in porous media* **2012,** *91*, (1), 101-121.

40. Spokoyny, F. E., Method and apparatus for the production of gaseous ammonia from a urea solution. In Google Patents: 2008.

41. Schell, L. P., Method of hydrolyzing urea contained in waste water streams. In Google Patents: 1978.

42. Wang, S.; Chen, C.; Shiau, B.; Harwell, J. H., In-situ CO 2 generation for EOR by using urea as a gas generation agent. *Fuel* **2018,** *217*, 499-507.

43. Bakhtiyarov, S. *Technology on in-situ gas generation to recover residual oil reserves*; New Mexico Institute Of Mining And Technology: 2008.

44. Kechut, N. I.; Jamiolahmady, M.; Sohrabi, M., Numerical simulation of experimental carbonated water injection (CWI) for improved oil recovery and CO2 storage. *Journal of Petroleum Science and Engineering* **2011,** *77*, (1), 111-120.

45. Fathollahi, A.; Rostami, B., Carbonated water injection: Effects of silica nanoparticles and operating pressure. *The Canadian Journal of Chemical Engineering* **2015,** *93*, (11), 1949-1956.

46. Alam, M.; Mahmoud, M.; Sibaweihi, N. In *A Slow Release CO 2 for Enhanced Oil Recovery in Carbonate Reservoirs*, SPE Middle East Oil & Gas Show and Conference, 2015; Society of Petroleum Engineers: 2015.

Appendix A: Representative Data

Table A. 1 Test #3

Time	Phase	Pump volume, ml	Oil volume, ml	Gas reading, ml	Gas level, ml
9/6/2018 20:29	Sea Water 3ml/min	248	0		99.4
9/6/2018 20:37	sea water 0.3 ml/min	230	0		99.4
9/6/2018 21:01		222.84	0		94.2
9/6/2018 21:34		213.08	3.6		85.4
9/6/2018 22:06		203.56	12		77
9/7/2018 10:06		180.34	21.2		67.8
9/7/2018 10:37		170.93	21.8		57.4

9/7/2018 11:25		156.61	22.2		42.4
9/7/2018 21:21		138.32	22.2		23.4
9/7/2018 21:24		138.25	22.4		75.4
9/8/2018 17:30		102.08	22.4		38.2
9/8/2018 21:06		95.57	22.4		31.8
9/8/2018 21:09		95.5	22.4		74.4
9/9/2018 10:00		72.14	22.4		50.4
9/9/2018 10:21		65.73	22.4		44.2
9/9/2018 10:47		59.4	22.4		36.2
9/9/2018 11:23		47.33	22.4		25.4
9/9/2018 15:06		40.66	22.4		18.8
9/9/2018 15:09	to urea	40.37	0	18	49.5
9/9/2018 15:42		30.7	0	28	39.8
9/9/2018 16:13		21.44	0	37	30.5
9/9/2018 16:22	to seawater	18.84	0	40	27.8
9/9/2018 16:43		12.41	0	46	21.2
9/9/2018 16:55		9.04	0	49	17.8
9/12/2018 12:49	to seawater	256.42	0	50	48.9
9/12/2018 13:41		241.86	0.2	67	34.2
9/12/2018 14:27		228.1	0.3	83	20.5
9/12/2018 14:31		226.79	0.4	13	19.1
9/12/2018 15:10		214.98	0.5	28	7.5
9/12/2018 15:13		214.29	0.5	29	44.7
9/12/2018 15:33		208.3	0.5	36	38.5
9/12/2018 20:43		198.67	0.6	47	28.8
9/12/2018 21:44		180.5	0.7	67	10.8
9/12/2018 21:47		180.31	0.8	17	42
9/13/2018 9:12		159.78	0.8	38	21.6
9/13/2018 9:40		151.65	0.8	46	13.7
9/13/2018 10:40		147.69	0.8	50	9.3
9/13/2018 13:40		147.65	0.8	50	28.1
9/13/2018 19:56		133.18	0.8	65	13.6
9/13/2018 20:00	to urea	132.86	0	8	49.3
9/13/2018 20:32		123.13	0	18	39.5
9/13/2018 21:16	to seawater	109.86	0	32	26
9/13/2018 21:40		102.8	0	39	18.9
9/13/2018 21:45		101.43	0	40	17.2
9/17/2018 9:25		99.69	0	41	49
9/17/2018 10:00		89.04	0	52	38.5
9/17/2018 10:32		79.53	0.1	65	28.9
9/17/2018 11:17		65.99	0.2	81	15.3
9/17/2018 12:30		63.63	0.2	84	13.2

9/17/2018 13:10	63.11	0.4	12	49
9/17/2018 13:45	50.5	0.4	23	36.4
9/17/2018 14:11	41.31	0.4	38	27
9/17/2018 14:30	24.64	0.4	56	10.5
9/17/2018 14:50	20.07	0.4	61	5.9

Table A. 2 Test #7

Time	Phase	Pump volume, ml	Oil volume, ml	Gas reading, ml	Gas level, ml
12/12/2017 14:43	Sea Water 3ml/min	262.34	0		100
12/12/2017 14:46		254.52	0		100
12/12/2017 15:10		247.73	0		94.4
12/12/2017 16:25		224.73	15		73.4
12/12/2017 17:04		213.07	22		57
12/12/2017 18:29		187.76	22		31
12/12/2017 18:33		187.38	22		44.4
12/13/2017 10:47		158.23	23.1		18.2
12/13/2017 10:53		157.98	0		50
12/13/2017 12:02		137.32	0		29
12/13/2017 13:56	To Urea	133.84	0	63	42
12/13/2017 15:45	To Seawater	101.82	0	30.5	16
12/13/2017 16:19	Stop	91.36	0	45	5.9
12/16/2017 10:16	To Sea water	90.39	0	6	49.9
12/16/2017 10:48	oil in plastic tubing	80	0	13	40.5
12/16/2017 10:53		79.42	0.5	18	38
12/16/2017 10:56		78.32	0.7	21	35.8
12/16/2017 11:07		74.99	0.8	25	32.1
12/16/2017 11:43		64.13	0.8	37	21.7
12/16/2017 16:32		55.35	0.8	48	40
12/17/2017 10:47		22.49	1.1	85	5.9
12/17/2017 11:06		170.85	1.1	7.5	42
12/17/2017 0:39		142.84	1.1	33	19.3
12/17/2017 13:03	To Sea water	135.67	1.1	40	12.3
12/17/2017 13:36	Stop	125.76	1.1	51	2.1
12/20/2017 10:43	Resume seawater	125.28	0	5	49.9
12/20/2017 10:43		113.68	0.2	12	38.1
12/20/2017 11:42		107.64	0.2	24	32.5
12/20/2017 12:15		98.09	0.2	35	22.6
12/21/2017 10:23	Stop	58.24	0.2	80	11.3

Table A. 3 Test #10

Time	Phase	Pump volume, ml	Oil volume, ml	Gas reading, ml	Gas level, ml
6/18/2018 11:14	Sea Water 3ml/min	246.53	0	16	99.2
6/18/2018 11:16	sea water 0.3 ml/min	239.24	0	16	99
6/18/2018 11:34		234.04	0	29	94
6/18/2018 14:10		228.96	4	32	88
6/18/2018 15:03		213.12	16.4	43	72
6/18/2018 15:46		200.3	20	73	58.6
6/18/2018 16:35		185.67	20.4	100	44
6/18/2018 16:40		184.21	20.4	12	42.4
6/18/2018 21:19		175.5	20.8	34	33.2
6/18/2018 21:23		175.11	20.8	35	76.4
6/19/2018 9:51		152.7	21.2	100	53.8
6/19/2018 10:38		138.63	21.2	10	40
6/19/2018 11:14		127.81	21.2	38	28.8
6/19/2018 11:40		119.93	21.2	60	20.6
6/19/2018 11:42		119.25	21.2	61	76.2
6/19/2018 13:00		95.99	21.2	100	52.4
6/19/2018 13:53		80.4	21.4	12	36.2
6/19/2018 16:20		75.99	21.4	24	32
6/19/2018 20:50		67.88	21.4	44	24
6/19/2018 21:10		62.1	21.4	58	18
6/19/2018 21:13		61.23	21.4	15	74
6/20/2018 9:32		38.47	21.4	68	50.8
6/20/2018 9:43	to urea	36.39	0	8	49.5
6/20/2018 9:50		34.23	0	10	48
6/20/2018 10:45		19.6	0	25	32.3
6/20/2018 10:59		13.87	0	31	26.7
6/20/2018 11:00	to sea water	13.55	0	32	26
6/20/2018 11:17		8.42	0	37	21
6/20/2018 11:33		3.48	0	42	15.9
6/23/2018 11:49	to sea water	253.52	0	43	49.6
6/23/2018 14:50		247.91	0	48	43.9
6/23/2018 15:29		236.2	0.1	62	33.2
6/23/2018 16:11		223.68	0.2	75	20.4
6/23/2018 16:58		209.52	0.2	26	6.3
6/23/2018 17:00		208.97	0.2	27	48.2
6/23/2018 17:57		192.19	0.2	46	31

6/23/2018 19:34		189.12	0.2	49	28
6/23/2018 20:06		179.42	0.2	59	18.4
6/23/2018 20:41		169	0.2	70	8
6/23/2018 20:47	to urea	167.37	0	10	49.1
6/23/2018 21:22		156.6	0	16	38.5
6/23/2018 21:55		146.9	0	26	28.7
6/23/2018 22:00	to sea water	145.65	0	27	28.3
6/23/2018 22:31		136.47	0	37	17.7
6/23/2018 22:35		135.41	0	38	16.7
6/26/2018 14:25	to sea water	134.19	0	38	48.6
6/26/2018 15:05		121.51	0	53	35.8
6/26/2018 15:44		109.83	0.2	66	24
6/26/2018 16:13		101.07	0.2	78	15
6/26/2018 16:16		101.01	0.2	5	48.7
6/26/2018 21:18		91.94	0.2	10	39.7
6/27/2018 9:47		69.4	0.2	42	17.2
6/27/2018 10:28		57.17	0.3	55	5
6/27/2018 10:29		56.74	0.3	56	40.5
6/27/2018 11:16		42.75	0.3	70	26.1
6/27/2018 11:49		33.15	0.3	80	16.3
6/27/2018 12:43		31.35	0.3	81	14.5
6/27/2018 12:51		29.23	0.3	84	12.3